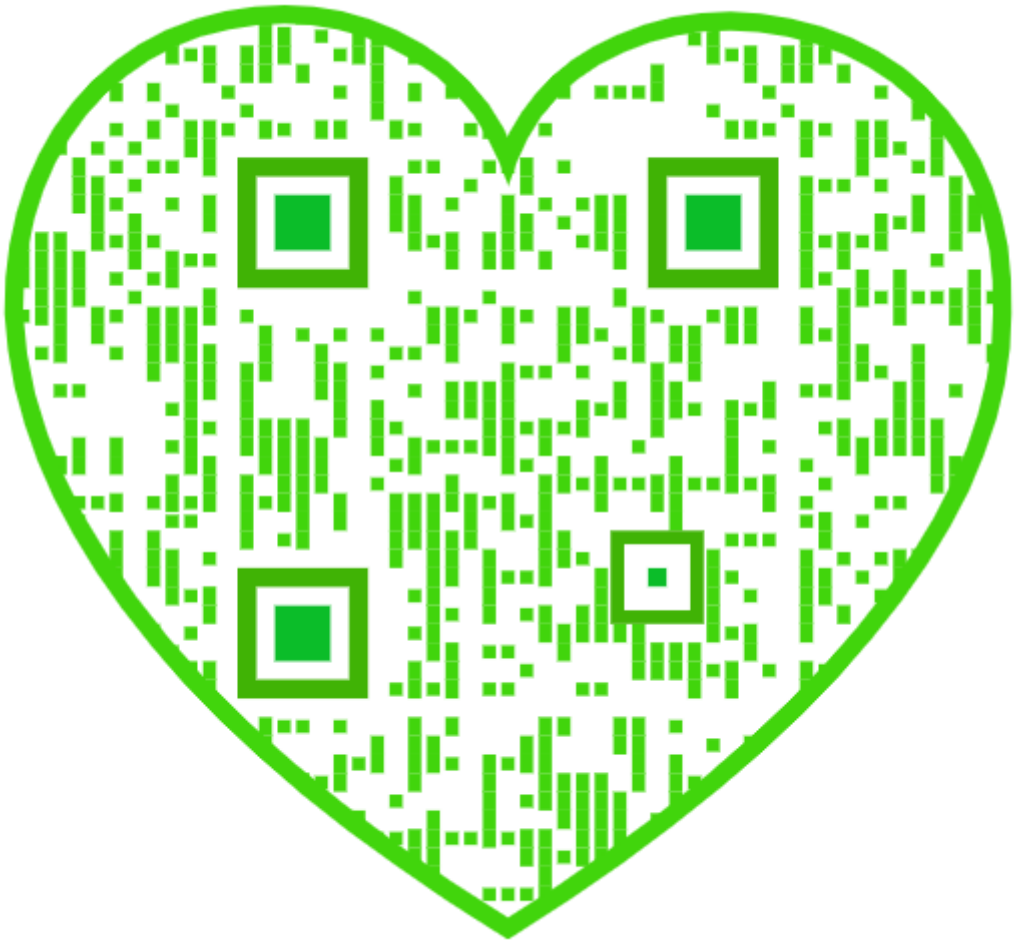
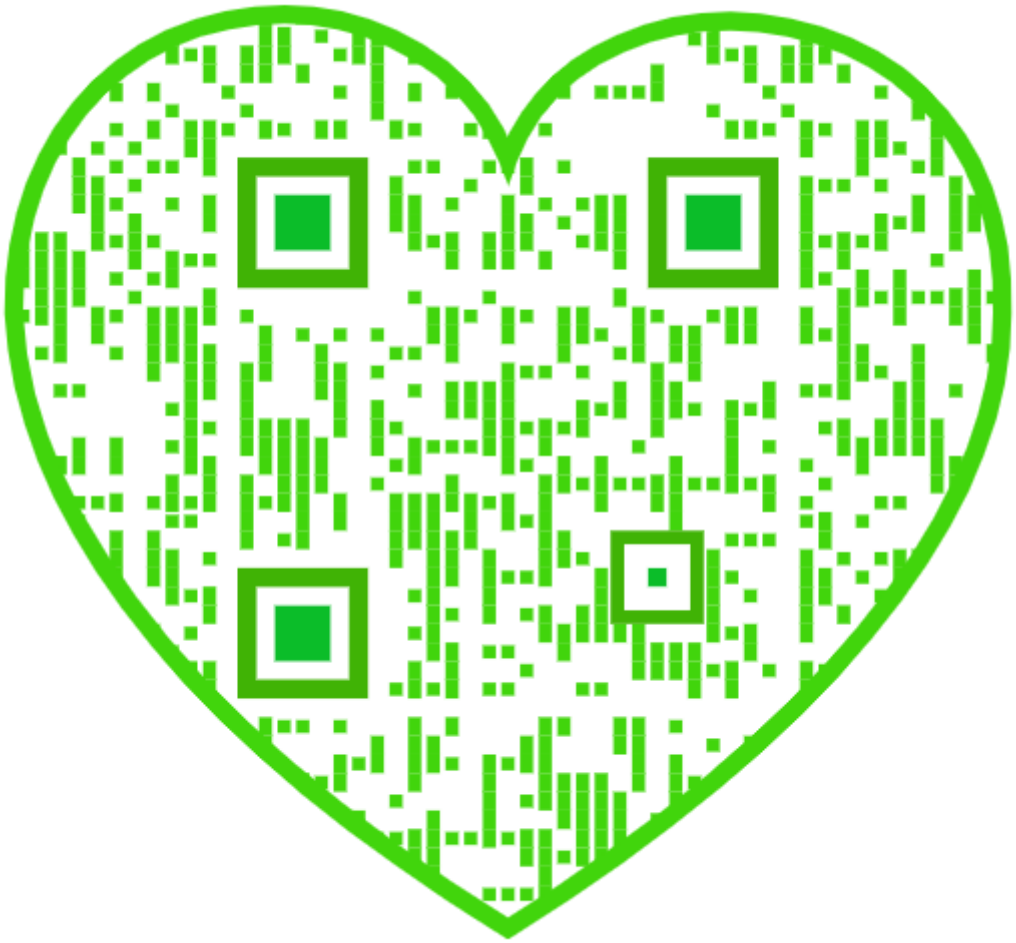




THEORETICAL AND PHYSICAL

CHEMISTRY

BY

S. LAWRENCE BIGELOW, PH.D.

PROFESSOR OF GENERAL AND PHYSICAL CHEMISTRY
IN THE UNIVERSITY OF MICHIGAN

NEW YORK

THE CENTURY CO.

1914

COPYRIGHT, 1912,
BY
THE CENTURY CO.

Published, February, 1912.

Chemical Library
QD
453
.B5
1914
cop. 2

PREFACE

MANY fundamental principles which apply in all branches of chemistry are given in the first course, but, of necessity, they are presented more or less didactically. Students at that time have so small a knowledge of the facts of chemistry they cannot be expected to understand the full significance of these principles, and they usually forget them quickly. In the sophomore or junior year conditions are otherwise, and at this stage they appreciate a critical consideration of these half-learned, three-quarters forgotten, fundamental principles, and both value and enjoy following the reasonings which lead to others. Such critical studies develop the habit of right thought and tend to diminish the number of those who memorize and recite parrot-fashion but will not think. For these reasons the writer believes a course of lectures in elementary theoretical and physical chemistry should follow the first courses in general chemistry and qualitative analysis.

This book is intended for use in such a course and is addressed to students who know a little chemistry. It comprises about all that can be advantageously presented in two or three lectures a week through one year, but it is hoped it may be found useful for shorter courses or collateral reading.

An unfortunate impression has got abroad that much mathematics is needed for a comprehension of physical chemistry; unfortunate, as it deters many who want it, and would profit by it, from electing the subject. No attempt has been made to avoid the use of mathematics, but a perusal of this book will show that ordinary arithmetic and elementary algebra are sufficient, except in five or six demonstrations. One unfamiliar with the calculus must take it on faith that steps in the derivations of half a dozen formulæ are correct, and that is all.

Classifications and methods of presentation which have proved satisfactory by their results should not be tampered with unless for clearly good cause. My colleagues will therefore recognize many familiar statements and arrangements in the following pages. But

C 5506

the book is not wholly devoid of novelties. In lecturing over this ground repeatedly for the last thirteen years, the facts arranged themselves, automatically as it were, in four subdivisions. The first section (three chapters) aims to show the value of philosophy in science. In the second section (seven chapters) the ever-present question is: What are the ultimate constituents? In the third section (nine chapters) we are, primarily, studying the properties of substances as such, and in the last section (eleven chapters) our attention is centered upon the processes by which substances become what they are.

The most difficult part of the task has been the selection of topics to omit. The title of almost every chapter is the title of a book, some of them works in several volumes. The attempt was made to select the salient facts and principles of each branch, and to construct from these a picture, intended to give a fair idea of the character of the information to be obtained by pursuing each subject further.

Believing it to be generally true that the value of items of knowledge is directly proportional to the simplicity with which they can be presented, most earnest efforts have been directed to show the inherent simplicity of some ideas, too often hermetically sealed under forbidding names and a maze of technical terms. Some may feel that this has resulted in too great disregard of a few time-honored terms, perhaps even a ruthlessness with one or two accepted elaborations. Criticism on this score will not be disagreeable, rather the reverse; for it is the plain duty of teachers and writers to make the truths and thoughts they have to impart as simple as they can. Ideas surrounded by a fog of terms and formulæ, through which only a select few can find the way, are open to suspicion as to their worth. We are obliged to coin too many new terms as it is, and any multiplication of them, not absolutely necessary, tends to establish a sort of monopoly which is abhorrent to the ideals of science.

It is with great gratitude that I acknowledge my indebtedness to my former teachers, Wilhelm Ostwald and Walther Nernst, whose writings I have freely used. It gives me pleasure also to acknowledge my obligations to my colleagues, Professors W. J. Hale, W. G. Smeaton and S. C. Lind for assistance and suggestions during the reading of proof.

S. LAWRENCE BIGELOW.

ANN ARBOR, MICH.
January, 1912.

CONTENTS

SECTION I

THE PRINCIPLES OF SCIENCE

CHAPTER — PAGE

1. **The Name, Scope and Value of Our Subject** 3

2. **The Scientific Method** 8

Subjective and Objective — Sense Impressions — Right Thought — Law — Cause — Theory — Induction — Deduction — Probability — Comparison of Laws and Theories — The Scientific Method.

3. **Fundamental Definitions** 17

Properties or Attributes — Object — Space — Dimensions — Time — Motion — Velocity — Acceleration — Inertia — Relativity Principle — Energy — Substance — Identity — Processes — Classification of Energies — Table of Energies and their Factors — Conservation of Energy — First Law of Thermodynamics — Perpetual Motion — Total Energy — Available Energy — Free Energy — Reversible Processes — Second Law of Thermodynamics — Matter — Weight — — Mass — Conservation of Mass — Units — Conditions of Aggregation — Gas Laws — Isotherm — Isobar — Absolute Zero — Isochor — Thermometers — Heat Units — Liquid — Solid — Solution — Solvent and Solute — Principle of Continuity — Melting Point — Classifications are Artificial.

SECTION II

STOICHEIOMETRY

4. **Unit Quantities of Chemistry and Chemical Notation** 39

Stoicheiometry — Chemical Compound — Element — Combining Weight — Law of Definite and Multiple Proportions by Weight — Law of Combining Volumes — Historical — Symbols — Formulæ — Equations — Symbol Weights — Formula Volume — Numerical Value of the Formula Volume — Rule for Formula Weight — Empirical Formulæ.

CHAPTER PAGE

5. **The Atomic and Molecular Theories** 56

Historical — Continuity and Discontinuity — Ultimate Constituents Unknowable — Dalton's Contributions — Atomic Weight — Usefulness of the Theory — Kekulé's Estimate — Atomic Theory Delayed Progress — Early Difficulties — Development of the Molecular Theory — Avogadro's Theory — Definition of Molecule — Definition of Atom — Determination of Molecular Weights — Dulong and Petit's Law — Atomic Heat.

6. **Chemical Energy, Affinity and Valence** 68

Definition of Chemical Energy — Affinity Tables — Velocity of Reaction — Law of Mass Action — Chemical Equilibrium — Strength of Acids — Equivalence — Maximum Work — The Dualistic Theory — Gravitation Analogy — Adhesion and Cohesion — Division into Factors — Intensity Factor — Capacity Factor — Unit of Combining Capacity — Equivalent Weights — Definition of Valence — Varying Valence — Structural Formulæ — Differences of State — Allotropy — Polymorphous Forms — Isomers — Polymers — Metamers — Atoms in Fixed Positions — Constitutive Properties — Conventions — Classification of Organic Chemistry.

7. **The Periodic System** 87

Prout's Hypothesis — Doebereiner's Triads — Law of Octaves — The Periodic Table — Chemical Properties — Physical Properties — The Periodic Law — Numerical Regularities — Usefulness of Law and Table — Exceptions to the Law — Other Graphical Representations — Protyle.

8. **Spectroscopic Evidences and the Theory of Inorganic Evolution** 98

Refraction of Light — Dispersion — Spectrum — Wave Lengths — Stefan's Law — Bolometer — Wien's Law — Star Temperatures — Line Spectra — Spectroscopic Analysis — Crookes' Tubes — Reversal of Lines — Kirchhoff's Law — Doppler Effect — Double Stars — Dark Stars — Absorption Bands — Carbon-monoxide Poisoning — Delicacy of Spectroscopic Methods — Spectra of Compounds — Spectra of Argon, Iron, Hydrogen — Formulation of Series — Spectra and the Periodic Law — Stellar Evidence — Dissociated Elements — Proto Elements — Dissociation of Iron — Zeeman Effect — Charged Corpuscles Hypothesis — Elements Complicated Compounds.

9. **Luminiferous Ether and Vortex Rings** 110

Luminiferous Ether — Electromagnetic Theory — Difficulties — Nature of Luminiferous Ether — Vortex Ring Hypothesis — Energy View.

CHAPTER PAGE

10. **Radioactivity and the Electron Theory** 113

Historical — Apparatus — Cathode Rays — Absorption of X-Rays — Fluorescent Screens — Canal Rays — Nature of the Cathode Rays — Velocity of the Particles — Value of e/m — Comparison with Hydrogen Ion — Charge on a Corpuscle — Stokes' Law — Mass of a Corpuscle — Nature of the Anode Rays — Nature of X-Rays — Radioactivity — Electroscope — Polonium — Radium — Actinium — Properties of Rays from Radium — Nature of the Rays — Evolution of Helium — New Elements — Application of Law of Mass Action — Half Period — Range of Rays — Rutherford's Table — Is Radium an Element? — Evolution of Heat — Heat of the Earth — Rutherford's Hypothesis — Delta Ravs — End Product of Disintegration — Other Radioactive Substances — Induced Radioactivity — Stability of Elements — Dynamides — Apparent Mass due to Electric Charge — Kaufmann's Results — Electron — Atoms — Electron Theory Offers Plausible Explanations — Faraday's Opinion.

SECTION III

PROPERTIES

11. **Gases** 135

Kinetic Theory — Facts to be Explained — Formulation — Heat a Mode of Molecular Motion — Absolute Zero — Chemical Action at Low Temperatures — Deduction of the Gas Laws — Deduction of Avogadro's Theory — Velocity of Diffusion — Fractional Diffusion — Velocity of a Molecule — Mean Free Path — Size of a Molecule — Estimates by Other Methods — Brownian Movement — Comparison of our Measurements — Extension of the Kinetic Theory — Conduction of Heat by Gases — Specific Heat of Gases — Molecular Heats — The Ratio, C_p/C_v — Monatomic Gases — Exceptions to the Gas Laws — Andrews' Isotherms — Van der Waals' Equation.

12. **Vapor Densities** 159

Dumas Method — Hofmann Method — Victor Meyer Method — Bleier and Kohn or Lumsden Method — Abnormal Vapor Densities — Calculating the Degree of Dissociation — Conduction of Heat by Dissociated Gases.

13. **Liquids** 175

Density — Specific Volume — Molecular Volume — Corresponding Conditions — Kopp's Results — Atomic Volumes within Molecules of Liquids — Covolume — Application to Selecting Molecular Weights — Association — Surface Tension — Capillary Phenomena — Jurin's Law — Definition of Critical Temperature — Surface Tension and Mutual Solubilities — Surface Tension and Vapor Pressure

CHAPTER PAGE

— Surface Tension of Solutions — Molecular Weights of Pure Liquids — Association — Internal Friction or Viscosity — Viscosimeters — Lubrication — Viscosity and Constitution — Viscosity of Salt Solutions — Viscosity of Gases.

14. Index of Refraction 190

Refractometers — Pulfrich Refractometer — Formula — Le Blanc's Method for Solids — Specific Refraction — Lorentz and Lorenz Formula — Molecular Refraction — Atomic Refraction — Atomic Refraction and Atomic Weight.

15. Solids 196

Nothing Absolutely Solid — Two Classes of Solids — Crystallography — Classification of Crystals — The First Law of Crystallography — Goniometer — Isomorphism — Isomorphism of Elements — Test for Isomorphism — Isomorphism and Analysis — Polymorphism — Properties of Crystals — Isotropic and Anisotropic Substances — Double Refraction — Polarized Light — Optical Axes — Nicol Prism — Polariscope — Crystals in Polarized Light — Rotation of the Plane of Polarized Light — Inferences from Crystal Forms — "Etch-Figures" — Liquid Crystals — Molecular Volumes of Solids — The Covolume of Solids.

16. Solutions I. — Osmotic Phenomena and the Theory of Dissociation in Solution 206

Classification of Solutions — Gaseous Solutions — Diffusion — Liquid Solutions — Dilute Solutions — Diffusion of Solutes — Semipermeable Membranes — Osmosis — Maximum Osmotic Pressure — Pfeffer's Apparatus — Plasmolysis — Isotonic Solutions — Van't Hoff's Generalization — Experimental Verification — Colligative Properties — Molecular Weights — Diffusion as a Method of Measurement — Diffusion through Jellies — Osmotic Pressures in Other Solvents than Water — Attempts to Explain Osmosis — The Kinetic Hypothesis — Arguments for and against the Kinetic Hypothesis—The Attraction Hypothesis—Argument for and against the Attraction Hypothesis — Surface Tension Hypothesis — The Function of the Membrane — Capillary Structure — Membranes as Solvents — Abnormal Osmotic Pressures — The Isotonic Coefficient — Electrolytic Dissociation Theory — Analogy with Gaseous Dissociation — Electrolytes — Number of Charges — Electrons — Indicating Ions — Similarity between Ions and Molecules — Explanation of Abnormal Osmotic Pressures.

17. Solutions II. — Rotation of the Plane of Polarized Light 226

Polariscope — Rotary Dispersion — Half-shadow Device — Solutions which Rotate the Plane — Rotating Power a Constitutive

CHAPTER PAGE

Property — Effect of Temperature — Specific Rotation of Pure Liquids — Specific Rotation of Solutions — Molecular Rotation — Multirotation or Birotation — Applications of the Polariscope — Sugar Analysis — Saccharimeters — Wedge Instruments — Use of White Light — Optical Activity — Optical Symmetry — Methods to Separate the Two Optically Active Varieties — Stereochemistry — The Asymmetric Carbon Atom — Compensation within the Molecule — Other Asymmetric Atoms — Asymmetric Molecules — Electromagnetic Rotation.

18. Solutions III. — Solid Solutions 237

Solutions of Solids in Solids — Isodimorphism — Double Salts — Solutions of Liquids in Solids — Solutions of Gases in Solids — Diffusion in Solids — Alloys — Glass and Dyed Fibers — Osmotic Pressure in Solid Solutions — Adsorption — Catalytic Effect of Metals — Adsorption of Liquids — Adsorption of Dissolved Substances.

19. Solutions IV. — Colloidal Solutions 243

Historical — Colloids and Crystalloids — Dialysis — Other Membranes — Other Colloids — Effort to Delimit Colloidal Solutions — Present Usage of the Term — Hydrosol and Hydrogel — Diffusion Through Hydrogels — Structure of "Gels" — Coagulation — Agglutination — "Protecting" Colloids — Colloidal Metals — Ultramicroscopic Method — Tyndall Effect — Size of Particles — Nomenclature — Osmotic Pressures of Colloidal Solutions.

SECTION IV

PROCESSES

20. Liquefaction of Gases 253

Different Kinds of Processes — The Liquefaction of Gases — Adiabatic Expansions — Experimental Determination of Critical Temperatures — Experimental Determination of Critical Pressures — Critical Concentration — Table of Critical Constants — Liquefaction of Air — Dewar Vacuum-jacketed Vessels — Thomson-Joule Effect — Application to Andrews' Isotherms — Uses for Liquid Air — Isothermal Compression — Gibbs' Phase Law — System — Equilibrium — Phase — Homogeneous and Heterogeneous Equilibrium — Component — "Order" of Equilibrium — Degrees of Freedom — Application to Isothermal Liquefaction — Supercooling — Stable and Metastable Equilibrium — Superheating — Prolongations of the Isotherm — Application of Van der Waals' Equation — Labile State — "Complete" Equilibrium — Mobile Equilibrium — Calculation of the Critical Constants — Law of Corresponding Conditions — The Reduced Equation of Conditions.

CHAPTER PAGE

21. **Vapor Pressure** 274

Measurement of Vapor Pressure — Static Method — Vapor Pressure Curves — Application of the Phase Law — Application of the Kinetic Theory — Balanced Action — Evaporation — Heat of Vaporization — Molecular Heat of Vaporization — Boiling Point — Ebullition — Graphical Representation of Boiling Points — Dynamic Method of Measuring Vapor Pressure — Determination of the Boiling Point — Regularities in Boiling Points — Boiling Point and Critical Temperature — Trouton's Law — Melting Point — Freezing Point — Determination of the Melting Point — Heat of Liquefaction — Molecular Heat of Liquefaction — Vapor Pressure at the Melting Point — Graphical Representation — Metastable Conditions — Experimental Demonstration of Supercooling — Superheated Solid Never Obtained — Sublimation — Heat of Sublimation — Boiling Point Below the Melting Point — Volume Change — Effect of Pressure on the Melting Point — Triple Point — Terminology — Transformations — Transition Points — Determination of Transition Points — Heat of Transformation — Graphical Representation — Other Triple Points — Transformation of Tin — Velocity of Transformation — Unknown Transition Points — Least Stable Variety Forms First — Solidification may Follow Melting — Monotropy and Enantiotropy — Thermodynamic Potential.

22. **Some Elementary Thermodynamic Deductions** 297

Formulation of the First Law — Work Done by a Gas Expanding Isothermally — Amount of Heat which can be Converted to Work — Economic Coefficient — Calculation of Heat of Vaporization — Calculation of Change of Melting Point upon Change of Pressure — Temperature Coefficient.

23. **Vapor Pressure of Solutions** 307

Theory of Fractional Distillation — Mixtures with Constant Boiling Points — When Vapor Pressure of the Solute is Negligible — Historical — Formulation — Improved Formula — Molecular Raising of the Boiling Point — Beckmann's Thermometer — Boiling-point Method — Other Forms of Apparatus — Precautions and Sources of Error — Landsberger-Walker-Lumsden Method — Menzies' Method — Measurement of Electrolytic Dissociation by the Boiling-point Method — Freezing-point Method — The Apparatus — Determining the Freezing Point — Precautions and Sources of Error — Lowering of Vapor Pressure and Osmotic Pressure — Calculating Molecular Lowering of Freezing Point — Calculating Molecular Raising of Boiling Point.

24. **The Process of Solution and Precipitation** 331

Solution Pressure — Solubility — Precipitation Pressure — The Solution of Gases — Henry's Law — Coefficient of Solubility — Bun-

CHAPTER PAGE

sen's Coefficient of Absorption — Dalton's Extension of Henry's Law — The Solution of Liquids — The Critical Point of Solubility — An Empirical Rule Regarding Solubility — Nothing Absolutely Insoluble — The Change of Solubility with Change of Temperature — Solubility Curves — Van't Hoff's Law of Mobile Equilibrium — The Change of Solubility with Change of Pressure — Le Chatelier's Law — Cooling Effect of Dissolving — Sometimes a Heat Effect — Solution in Part a Chemical Reaction — Not Sure what we have in Solution — Solubility of Sodium Sulphate and its Hydrates — Cryohydric Points — Cryohydrates — Continuity of Properties of Solutions Passing Transition Points — Inclinations of the Curves — Application of Gibbs' Phase Law — Quadruple Points — Freezing Mixtures — Mechanism of Freezing Mixtures — Solubilities of Ferric-chloride Hydrates — Eutectic Mixtures — Distribution or Partition Coefficient — Extraction.

25. Velocities of Chemical Reactions 352

Chemical Kinetics and Chemical Statics — Heterogeneous and Homogeneous Systems — Law of Mass Action — Inversion of Sugar — Formulation — The Velocity Constant — Reactions of the First Order — Other Unimolecular Reactions — Theory — Reactions of the Second Order — Formulation — Experimental Verification — Other Bimolecular Reactions — General Characteristic of Second-order Reactions — Reactions of the Third Order — Formulation — Other Reactions of the Third Order — In General Regarding Third-order Reactions — Determining the Order of a Reaction — Reactions of Higher Orders — General Formulation — Most Reactions of Low Order — Heterogeneous Systems and the Law of Mass Action — Influence of Temperature on Velocity of Reaction — Kindling Temperature — Spontaneous Combustion — Catalysis — Influence of Solvent — Extent of Catalytic Effect — Autocatalysis — Enzymes — Negative Catalysis — Explanations of Catalytic Effects.

26. Equilibria in Chemical Reactions 371

All Reactions Reversible — Formulation of Equilibrium — Classification — Order of Equilibrium — Heterogeneous Physical Equilibria — Exceptions to Henry's Law — Inferences Regarding Association, Dissociation, etc. — Other Physical Equilibria — Homogeneous Equilibrium in the Gaseous Phase — Effect of Pressure — Dissociation Constant — Effect of the Presence of One of the Products of Dissociation — Homogeneous Equilibrium in Liquids — Quantitative Calculation — Effect of Adding One of the Products of the Reaction — Effect of Change in Volume — Homogeneous Equilibrium in Solutions — Ostwald's Dilution Law — An Empirical Formula — Color of Ions — Numerical Values of Dissociation Constants — Strength of Acids — Division of a Base between Two Acids — Affinity Constants — Effect of Adding More of One Ion — Qualitative Experiments —

CHAPTER PAGE

Quantitative Application — Reduction of Acidity — Hydrolysis — Theory of Indicators — Homogeneous Equilibrium in a Solid Phase — Chemical Equilibria in Heterogeneous Systems — Solubility Product — Formulation — Exceptions — Complex Ions — Increasing the Solubility — Dissociation of Complex Ions — Heterogeneous Chemical Equilibria between Solids and Gases — Dissociation Pressure — Water of Crystallization — Efflorescence — Water Vapor, Hydrogen and Iron — Effect of Temperature on Equilibrium — Catalysis and Equilibrium.

27. Thermochemical Data **404**

Factors of Heat Energy — Units — Apparatus and General Methods — Water Calorimeter — Heat Capacity of Apparatus — Determination of Heat Neutralization — Bomb Calorimeter — Ice Calorimeter — Steam Calorimeter — Thermometers — Heat of Reaction — Heat of Combustion — Heat of Formation, Neutralization, Solution, Dilution, Fusion, Vaporization — The First Law of Thermochemistry — Law of Constant Heat Summation — Energy Equations — Use of Energy Equations — Calculation of the Heats of Reactions — Some Thermochemical Data — Allotropic Forms — Organic Compounds — Effect of a Change in Volume — Only Initial and Final Conditions need be Considered — "Heat Effect" — Heats of Combustion and of Formation of Homologous Series — Heats of Organic Reactions — Thermoneutrality — Heat of Neutralization a Constant — Heat of Formation of Water from its Ions — Heat of Dissociation — Principle of Maximum Work — Contradictions of the Principle — Le Chatelier's Law — The Law does not enable us to Foretell Chemical Occurrences.

28. Electrochemistry I. — The Quantity Factor **423**

The Galvanometer — Ampère's Rule — Resistance — Ohm's Law — Units — Methods of Measurement — Fall in Potential — Calculating the Current in a Branching Circuit — Wheatstone Bridge — Conductors and Non-Conductors — Classification of Conductors — Faraday's Law — The Faraday — Coulometers — Current Density — The Conductivity Method — Specific Resistance or Resistivity — Specific Conductance or Conductivity — Capacity Factor of a Cell — Molecular Conductivity — "Infinite" Dilution — Equivalent Conductivity — Effect of Temperature — Degree of Dissociation — Rate of Migration of Ions — Complex Ions — Kohlrausch's Rule — Actual Velocity of Ions — Effect of Viscosity on the Velocity of Ions — "Electrical Endosmosis" — Cataphoresis — Electrostenolysis — Ostwald's Dilution Law and the Dissociation Constant — The Dissociation Constant and Chemical Constitution — Calculating the Dilutions at which Two Acids are equally Dissociated — Calculating Dilution Necessary for a Definite Degree of Dissociation — Isohydric Solutions — The Basicity of Acids — Use of the Basicity

CHAPTER PAGE

Rule to Determine the Molecular Formula — Pure Water — Degree of Dissociation of Water — Determining Solubility of Difficultly Soluble Salts — The "Hardness" of Water — Conductivity of Non-aqueous Solutions — Dielectric Constant — Conductivity of Solid and Fused Salts.

29. Electrochemistry II. — The Intensity Factor 466

Electromotive Force — Measuring Electromotive Force — Poggendorff Compensation Method — Potentiometer — Cadmium Standard Cell — Zinc Standard Cell — The Electrometer — Surface Tension of Mercury — Capillary Electrometer — The Double-layer Theory —Primary and Secondary Batteries — Reversible and Non-reversible Cells — Osmotic Theory of Production of Potential — Formula for Potential at an Electrode — Formula for Potential at Contact of Two Solutions — A Concentration Cell — Amalgam Electrodes — Gas Electrodes — Measurements of Single Potentials — Normal Electrode — Calomel Electrode — Potential Series — Oxidation and Reduction Series — Polarization — Measurement of Polarization — Measurement of Polarization at One Electrode — Decomposition Potentials — Intensity of Fixation of Ions — Application of these Principles to Analysis — Illustration of the Value of Theories — Relation between Chemical Energy and Electrical Energy — The Temperature Coefficient — Storage Cells — The Lead-sulphuric Acid Cell — The Efficiency of Storage Batteries — The Temperature Coefficient of Storage Cells — The Nickel-Alkali-Iron Cell.

30. Actinochemistry 502

Radiant Energy — Photochemical Absorption — Some Reactions Influenced by Light — Formation of Hydrochloric Acid — Photochemical Induction — Photochemical Extinction — Actinometers — Photography — Luminescence — Fluorescence — Phosphorescence.

Appendix 520

A Method for Calculating Changes in Gaseous Volumes — Use of Logarithms — Use of Exponents — Metric System and Some Equivalents — Miscellaneous Data and Formulæ.

Index 527

THEORETICAL AND PHYSICAL CHEMISTRY

Theoretical and Physical Chemistry

SECTION I

THE PRINCIPLES OF SCIENCE

CHAPTER I

THE NAME, SCOPE, AND VALUE OF OUR SUBJECT

THERE is a large and increasing body of classified knowledge, consisting of important facts, generalizations, and theories, which forms the basis for each and for all branches of the science of chemistry. Most of the recent books presenting this knowledge have called it "physical chemistry," because it contains so much that belongs equally to chemistry and to physics. This is neither a new name nor a new subject. Gilbert's "Annalen der Physik und der Physikalischen Chemie," in 1819, recognized, in this use of the term "physical chemistry," the claims of scientific investigations including facts from each of the two sister sciences.

But it has grown amazingly since then, and for the last twenty-five years has been accepted as a special branch of chemistry, quite on a par, in usefulness and in what it has accomplished, with other branches, such as organic or analytical chemistry. The extraordinary quantity and quality of the discoveries resulting from its pursuit are but inadequately presented in this book, and the reader is urged to refer to the standard works of Wilhelm Ostwald, often called the father of this specialty, and to the no less authoritative texts of W. Nernst and J. H. van't Hoff.*

* An interesting historical summary is contained in "An Introduction to the Study of Physical Chemistry" (47 pages), written by Sir William Ramsay as an introduction to a series of texts on special topics of physical chemistry of which he is the editor. It was bound in with the first copies of "The Phase Rule," by Alexander Findlay, but latterly has been prefixed to "Stoichiometry," by Sydney Young. It is also published separately.

Sometimes the term "physical chemistry" is used to denote a special group of laboratory methods, applying to chemical problems more refined measurements and more elaborate instruments than the older methods of descriptive inorganic, organic, or analytical chemistry. If it is to stand for this group of laboratory methods, we need another name for the more comprehensive subject, of which those methods are a subdivision.

W. Nernst calls his book "Theoretical Chemistry," but this is open to the objection that the subject covers much more than the theories alone. Without doubt, the best title is that which Ostwald gives it, "Allgemeine Chemie," "general chemistry," for it does comprise the facts, laws, and theories which are of general applicability throughout chemistry. But "general chemistry" has grown to mean a beginners' course, introducing a few main principles, and as much of descriptive inorganic chemistry as time permits. The tendency to increase the number of fundamental general principles in the first courses at the expense of the purely descriptive matter is more and more marked, until, in many cases, the first courses in chemistry to-day are very like the elementary courses in "physical chemistry" of ten or fifteen years ago. This welcome transformation is directly due to Ostwald's teaching and writings. But it gives the beginners' course an undeniable right to the title "general chemistry."

What then shall we call a course of lectures, or book, which strives to summarize and to unify the most important facts and ideas of physical, general, theoretical, historical, inorganic, organic, analytical, and applied chemistry, in short, of chemistry as a whole? Not many years ago, books with the above aim were called "chemical philosophies." Dalton's epoch-making book containing the first clear statement of the laws of definite and multiple proportions and the atomic theory, published in 1808, was called "A New System of Chemical Philosophy." In 1837, J. B. Dumas published his "Leçons sur la Philosophie Chimique." These instances might be multiplied.*

The term fell into disuse, if not disrepute, largely, no doubt, due

* On page 2, Dumas has this to say about his subject: "La philosophie chimique (a peine si j'ose la définir), a pour objet de remonter aux principes généraux de la science, de montrer non seulement en quoi ils consistent aujourd'hui, mais encore quelles sont les diverses phases par lesquelles ils ont passé, de donner l'explication la plus générale des phénomènes chimiques, d'établir la liaison qui existe entre les faits observés et la cause même de ces faits."

to the fact that philosophy passed through a stage of vague speculations, and no scientist could see any connection between such vaporings and his own exact measurements. But real philosophy has emerged from this eclipse and is to-day what it always purported to be, the science of sciences, with the great aim, the classification and unification of all knowledge.

Each special branch of chemistry contains a vast accumulation of details and some generalizations. Our subject makes a specialty of these generalizations. It stands in the same relation to the subdivisions of the science of chemistry in which philosophy stands toward all sciences. Its main object is to unify thought within the science of chemistry; therefore, it might well be named, the "philosophy of chemistry." Its task is then nothing less than the systematization of all chemical facts; its endeavor is to constitute itself a guide through all the ramifications of this most complex, most unfinished, and at the same time, most promising and most fascinating of sciences.

The value of the subject cannot be disputed. Partly review, partly entirely new to students at the stage at which it is customarily taken up, it gives, as it were, a bird's-eye view of what has been accomplished and what should be done next; it brings out interrelationships not before suspected, and opens vistas of possible new developments and applications which should produce an inspiring effect.

Searchingly critical in its spirit, no idea is so venerable it must be spared, and none so new it need not be considered. Its consistent and literal application of the scientific method has set many an old dogma tottering, to the extreme annoyance of the dogma's chief priests, and has exalted new ideas to a prominence yet more vexatious to the Pharisees of science. Worst offense of all, it claims to be a discipline containing all that is good of conservatism, in spite of the rapid advances of which it is the instigator.

The necessity for some acquaintance with this discipline, to the scientist and to those in other professions utilizing the facts and methods of chemistry, is self-evident and universally acknowledged. Perhaps it is unfortunate that one of its aliases is "theoretical chemistry," for there seems to be still some misunderstanding as to the practical value of theoretical chemistry for technical chemists. This misunderstanding is disappearing among employers, but it is still too evident among students at the stage when they have just decided to specialize in chemistry. This is doubtless due in part to

ignorance of the import of the word theoretical. Common usage seems to have affixed to it an undeserved stigma. One hears such phrases as, "Oh, well, that is only a theory," or, "He is merely a theoretical chemist," used as terms of opprobrium. Some self-styled "practical" men think theories useless, all very well in universities perhaps, but out of place in the factory. It is amusing to see such a man, confronted by a new problem, grope about for a "working hypothesis" to help him out. Perhaps the books on theoretical and physical chemistry are a little at fault, perhaps they do not convincingly enough teach the value and usefulness of theories. One sometimes hears the objection that they are written by those for whom the theories and generalizations are ends in themselves, and so not enough emphasis is laid on the applications. There may be some truth in this, but there is often more truth in a quite opposite view. Feeling the pressure to prove the subject of practical value, knowing the many important facts he has to relate and the limited time and space at his disposal, a writer is apt to pass over the older and most fundamental topics too rapidly. If he made haste more slowly, relied a little less on the previous knowledge of his readers, took the opportunity that this previous knowledge gives him to examine critically and at some length the dogmatic statements learned hurriedly in earlier courses, the "practical" worth of the knowledge itself, and of the habit of criticism it cultivates, might be more evident. At the same time the student would acquire that familiarity with the main generalizations which must precede their quick and effective application to new problems.

A difficulty with which a teacher must contend is often the mental attitude of the student. He is, as a rule, impatient of all except what he plainly sees can be converted into "bread and butter," and forgets that a man with very little previous mental training can learn how to carry out any established, routine, process according to directions, and that the higher prizes are for those with trained minds as well as hands, who can think and improve processes or invent new ones. Only too frequently he seems determined to qualify for a clerkship rather than make the effort to deserve managerial responsibility; to become an artisan rather than a scientist. He is young and inexperienced and not the best judge of what he needs, but he seldom lacks confidence in his own powers of selection.

Theory is to practical application as thought is to action, and the "practical" chemist, who considers theoretical chemistry unnecessary

in his business, is in the ludicrous position of one advocating action without thought.*

The case for theories and our whole subject, indeed, may be summarized in a few brief statements. Without theory there can be no imagination; without imagination there can be no originality, no advance. Therefore we must foster imagination and the theories which feed it. But unrestrained imagination has often led to false conclusions which have proved costly and wasteful of both time and money. We must, therefore, not be hasty but must curb the imagination carefully. The necessary curb is experiment and right thinking.

The principles of right thinking are the principles of science, and some acquaintance with these is a necessary part of a chemist's training.

* In a short sketch of the life of Lord Kelvin, formerly William Thomson, Professor Webster says: "It is interesting to recall, in connection with the first cable, which lived to transmit only 732 messages, that it was ruined by the practical, that is, nontheoretical electrician, Mr. Whitehouse, who applied to it currents from huge induction coils, probably giving potentials of two thousand volts. By the advice of Thomson, thus dearly paid for, this was reduced, on the 1865 cable, to a few volts, this being amply sufficient to work his delicate instruments." *Science*, 1908, p. 4.

CHAPTER II

THE SCIENTIFIC METHOD

Division into Subjective and Objective. The whole universe may be considered as divided into two parts; on the one hand, yourself, a being capable of making observations; on the other hand, everything you observe outside yourself. You may turn your attention inward and study your mental processes, your feelings, and your emotions, or you may turn it outward and study the external universe. The facts you learn regarding your mental processes are called subjective, those you learn regarding your surroundings are called objective. Objective knowledge is the result of perception, subjective knowledge is the result of reflection.

Sense Impressions. We depend then for our knowledge of the external universe on our senses; we receive sense impressions and these are items of objective knowlege. Sense impressions recorded as such, without regard to possible connections, constitute empirical knowledge. Our minds set to work sorting these items, and we are capable of following this sorting process and noting facts about it, thereby acquiring subjective knowledge.

The Mind an Instrument. The "natural" sciences, of which chemistry is an important member, are objective, based on observation and experiment. But the facts of observation and experiment are dealt with by the mind, by mental processes. Thus the mind is the ever present, most constantly used instrument in all sciences. We devote much time and care to learning how to use balances, thermometers, refractometers, polariscopes, and a whole multitude of other instruments. We should do well if we devoted more time to learning how to use the most important instrument of all, the mind. Surely a scientist, at least as much as anyone, needs to know how to use his head, how to classify his ideas, and how to appraise them. This is a science in itself — philosophy. Therefore, every scientist needs to know the fundamental principles of philosophy, some logic, and some metaphysics. Even if we wish merely to remember, we should learn to think systematically. The art of remembering is the

art of thinking, and the way to retain a fact is to establish relations, associations, between it and other similar facts already in the brain.

Right Thought. Right thinking establishes precisely such relations and consists in chains of reasoning, each link suggested by, and a necessary, or at least plausible, consequence of the one before. The scientific method consists of this right thinking based on, accompanied, and followed by laboratory experiments. By this method science has advanced; by this method it will advance. The system of generalizations and theories which we are taking up is one of its results and an illustration of its application. This method must be understood, learned, and practiced until it becomes a habit, part of one's self. The establishment of this habit is the chief aim of scientific education, for it is the most valuable asset a scientific man can have. There is nothing recondite about the method. It may be summed up in two words, common sense. But common sense, in this sense, is not so common as it should be.

Subjective Facts. There is an unjustifiable tendency among some scientists to insinuate that only results of laboratory experiments deserve the name "facts" and that such results comprise all knowledge. At one time those undesirable attributes, dogmatism and intolerance, were thought to be the special prerogatives of religious sects, but in our haste to prove our broadmindedness and other virtues, we have overshot the mark, and now the scientist intolerant of religious beliefs is a more frequent phenomenon than the theologian intolerant of real science. Man has observed the effects of ideas and of emotions on others and on himself, and has learned facts in this department, based on experience and experiments, as convincing and more intimate than those carried out in the chemical laboratory. He knows that all other facts are ultimately converted into material for the mind to deal with, and that it is in this cerebral laboratory, by means of its own mental methods, the crucial experiments are tried, the results of which spell success or failure, happiness or unhappiness.

Knowledge does not begin and end with the "physical" sciences and there is as much to be learned in metaphysics * as in the former.

Words and Ideas. We communicate ideas almost exclusively by words, spoken or written, and unfortunately the same words sometimes convey different ideas to different individuals. This is a pro-

* The term metaphysics is applied to subjects in which the facts examined are emotions, thoughts, and mental conditions. W. Whewell, "Novum Organon Renovatum," London, 1858, p. 139.

lific source of misunderstandings and errors. For instance, as was brought out in the first chapter, the word "theories" means fanciful and useless things to some, while to others it connotes about half the most absolutely necessary items of a "practical" man's mental outfit.

The customary method is for texts on science to plunge into the subject using many terms without defining them. The young student of chemistry soon talks freely of laws, theories, and causes, of energy, matter, weight, and mass without clear ideas of the significance of those terms. He gradually, and unconsciously, forms fixed, and too often erroneous, opinions about them, which stunt his mental development. He needs the chastening effect of a searching cross examination on what he means by those words.

Not many years ago students were obliged to study the classics and humanistics before beginning the "natural" sciences. They thus acquired knowledge of the meaning of words and of the existence of fundamental problems and this could be assumed in scientific texts. But the elective system has been creeping to lower and lower grades; such broadening studies may be completely avoided, and it is no longer safe to make that assumption.

Generalization, Formulation, Law. By a mental process we sort isolated bits of knowledge, obtained by observation and experiment, into groups, such that one feature is common to all the facts in one group, and we state this common feature in a sentence. For instance, we recognize it is true for many thousands of experiments that the elements unite in definite parts by weight, or in simple multiples of weights characteristic of the several elements, to form chemical compounds. This is the statement with which we are familiar as the law of definite and multiple proportions by weight, sometimes called the law of constant proportions. Since it is true for many cases we may call it a generalization. We may also describe it as a formulation of an observed regularity in the processes of nature. Its most familiar name is "law." Notice that a generalization, formulation, law is the result of sorting information in our minds; it is then a product of our minds, and in this sense the "laws of nature" are made by man.

A "law" in science is intended then to be a statement of fact, and it is so, unless, as sometimes happens, essential features of the experiments have escaped observation. It follows that nothing which is not fact, experimentally determined, should ever be called a law.

This last statement should be adopted as a fundamental principle, always to be observed, for infractions of this rule are sure to result in confusion and misunderstandings, in what is aptly called "muddy thinking."

If a student knows the correct definition for law and then hears the statement "equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules," called "Avogadro's Law," it is but natural for him to infer that we have seen and counted molecules; he is led to believe what is not so and the fault is not his. Precise definitions and correct use of words are necessary in classifying knowledge. Since science is classified knowledge, whoever thinks precise definitions of terms to be of secondary importance must consider science of but slight value.

Approximations Sometimes Called Laws. Our simple formulations may be imperfect, they may not even express accurately the experimental results. Our gas laws, for example, are formulations which do not correctly express the behavior of any known gas. We are perfectly well aware that they are only approximations, but still they are based directly upon facts, inasmuch as they express what we may call the limits towards which the actually observed and measured regularities in the behavior of gases seem to tend. Closer study, or better instruments, permitting more refined measurements, may enable us to improve our statements just as our gas laws are made to express the facts better by adding to them van der Waals' corrections.

Two Classes of Laws. Our laws may be divided into two categories: first, laws which express the facts so closely we are unable to measure any divergence; second, laws which are approximate formulations of the facts. Good examples of the first class are Newton's law of gravitation, the law of the conservation of energy, the second law of thermodynamics, the law of the conservation of mass, and the law of constant proportions by weight. The gas laws furnish typical instances of the second class.

Law a "Short Cut" in Education. The establishment of a law is to be welcomed as a distinct advance, for just as it is easier to remember one thing than many, so is it easier to remember a law than all the hundreds, perhaps thousands, of isolated instances. We are not apt to appreciate the value of our inheritance of knowledge condensed in our laws, for they are so quickly learned and seem so self-evident we forget the patient labors which invariably preceded their formulation. Embryology has taught us that the young of animals

in their early stages summarize the process of evolution which took years. Just so we mentally summarize the evolution of science in terms of these generalizations. The more the facts get condensed into generalizations the more rapidly can students pass through the necessary mental evolution and reach the frontier of our knowledge where the most important work is to be done.

Other Meanings of the Word Law. Law is a poor word for our purpose because it is also used for the enactments of legislative assemblies, which only too infrequently conform to the "laws of nature." "The civil law involves a command and a duty; the scientific law is a description, not a prescription." *

As Alexander Smith says, no penalty attaches to the gas which disobeys the gas laws, it is neither fined nor imprisoned.

> It is, therefore, . . . very misleading if we permit ourselves to say that Boyle's law "acts" so as to "cause" gases to behave in a certain way, or that the law "operates" to "produce" a certain behavior, or that other behavior is "impossible" to the gas, or that the law of cohesion "intervenes" when the gas is under low pressure, and causes its behavior to "diverge from that required" by Boyle's law, or to say that a gas "disobeys" Boyle's law. . . . Phrases like the above, common as their use is, have been selected apparently with a view to introducing a maximum of distortion and obscurity. . . . It is the gas that "acts" and gives rise to the making of Boyle's law, and the latter is only an epitome of the way it acts. . . . The progress of science would be almost completely arrested if, every time we succeeded in formulating a seemingly satisfactory statement of truth in regard to some set of phenomena, the exhibition by nature of any behavior which was in conflict with our statement became forthwith "impossible." . . . It is not the gas which "diverges" from our statement or "disobeys" our law, but our statement which is proved by the behavior of the gas to be inaccurate. Our procedure in such cases is always more logical than our language, for we never attempt to cure the gas of its error but always the law itself by suitable modification in its phraseology.†

It is a pity that the word is so ingrained in the whole literature of science that it is impractical, if not impossible, to avoid it entirely; but either generalization or formulation is a better term. These words are too long and we must make the best of it, remembering that the word "law" means one thing to a scientist in his subject and another thing to a policeman on duty.

Rules. We do have, in science, a number of rules which are very like legislative enactments, inasmuch as they are directions or guides for experiment, thought, or expression, voluntarily laid down by our-

* Karl Pearson, "The Grammar of Science," second edition, p. 87.

† Alexander Smith, "General Inorganic Chemistry," pp. 7 and 8.

selves because they are expedient; because following them brings order out of confusion, or saves time. We have already laid down a rule for ourselves: never give the name "law" to anything but statements of fact within the reach of direct experimental proof.

Cause. We do not rest content having grouped facts and obtained generalizations or laws. We ask ourselves what may be the reasons, the causes, the explanations for the observed facts, the laws. The words cause, effect, and explanation are used freely in daily conversation and in science, but we are hard put to it if pressed for their precise meaning. They open large questions which we cannot answer completely.

Hume first called attention to the fact that what we observe are sequences of events or conditions and that is all. The condition or event A we learn is followed by the condition or event B, and this by C and so on; or, when A, B, and C are in juxtaposition, the next thing we know, D has happened. But in the last analysis we cannot say *why* B should follow A, or C follows B, nor *why* A, B, and C, finding themselves together, give D. The actual connection, we cannot observe; it escapes us. Hydrogen and oxygen and a high temperature, brought together, furnish an explosion, but we don't know why. If nitrogen be substituted for oxygen, the explosion does not follow and we cannot account for the absence of the effect. We may say there is marked chemical affinity between hydrogen and oxygen and less between hydrogen and nitrogen, but this does not get us far, for at once the question rises, why is there this difference in affinities? We do not know. Every "explanation" raises a new question and we cannot give a complete answer to "why," for the simplest observed event.

That a certain sequence has occurred and recurred in the past is a matter of experience to which we give expression in the concept *causation;* that it will continue to recur in the future is a matter of belief to which we give expression in the concept *probability*. Science in no case can demonstrate any inherent necessity in a sequence, nor prove with absolute certainty that it must be repeated. Science for the past is a description, for the future a belief; it is not, and has never been, an explanation, if by this word is meant that science shows the *necessity* of any sequence of perceptions. Science cannot demonstrate that a cataclysm will not engulf the universe to-morrow, but it can prove that past experience, so far from providing a shred of evidence in favour of any such occurrence, does, even in the light of our ignorance of any necessity in the sequence of our perceptions, give an overwhelming probability against such a cataclysm.*

* Karl Pearson, "The Grammar of Science," second edition, 1900, p. 113.

This quotation presents a rather extreme view. If there were no "necessity" it would be just as likely that any weight of oxygen whatsoever should unite with one gram of hydrogen as that eight grams of oxygen should do so. If there were no "necessity" the chances would be almost vanishingly small that these exact proportions should be met in two or three successive experiments. They are met as often as we please to carry out the synthesis of water, therefore there is a "necessity," though we cannot state in what it consists.

There must be connection between cause and effect even though we cannot describe it, and we are justified in assigning reasons and offering explanations, but we must realize that none of our reasons are complete; that all our explanations are but partial. It is as if to each event were attached an immense number of threads extending back to all infinity. Now and then we can grasp a thread or two near the event but the others we cannot grasp. What we know regarding the simplest imaginable event is insignificant as compared to what we might know.

Theory. Having observed a fact or law, we ask ourselves what are the conditions, which, if they existed, would presumably give rise to what we observe. Final causes we cannot determine, but plausible, partial explanations of events are within our reach, and these are our theories. They are explanations, for we never should reach them if there were no connection at all; they are only partial explanations, for we have not a complete explanation for the simplest event; they are plausible only, for they may or may not represent actual conditions. Often we have a choice between alternative explanations for given facts, and we choose that which appears the more probable, all things considered. But new facts may some day cause us to modify our explanation, or substitute a new one, or may make one previously discarded seem the most plausible.

Nature of Theories. Characteristic of hypotheses and theories is that they do not state the results of observation and experiment. They may or may not express facts, which may or may not come within range of direct observations at some future time. To say you will prove a theory is a contradiction in terms. If you succeed in proving that the assumptions of some theory are facts, the statement becomes a statement of fact, or a law, and promptly ceases to be a theory.

Induction. The process thus far outlined, from experimental facts or sense impressions, through a mental classification to a generali-

zation, formulation, or law, and then the further mental process resulting in a theory, is what is called induction. This method of thought, from outer universe to ideas, figments of the imagination, is inductive reasoning.

The Use of Theories. Now laws and theories are the tools of thought wherewith a large range of phenomena may be grasped at once by one mind. Ability to think in these terms is the main distinction between the educated and the uneducated man.

Starting from the inner idea, we can reason outward and foretell what will probably result if we try the experiment. Our laws and theories enable us to prophesy, and that is a most useful faculty, if we can do it correctly. Those laws and theories which experience proves lead to conclusions justified by the event are the most valuable mental tools we can have, as no one will deny. Mere suggestions, based on inadequate evidence, perhaps on an isolated instance, frequently lead to erroneous conclusions, but unfortunately they too are often called theories. That is the reason the term theory has, as has been said, fallen into disrepute. There is a great difference, which ought to be accentuated by the use of different words, between such mere suggestions and the theories of science. A theory is not incorporated in the body of a science nor taught as part of that science until it has proved its usefulness as a tool by which to foretell future events.

Investigators never put things together haphazard, and then stand aside to see what will happen. They reason things out with the assistance of their theories and generalizations and plan their experiments to confirm or overthrow some working hypothesis. Thus old and tried theories are in constant use. A working hypothesis gains in reliability each time prophecy based upon it is found correct, and after enough such demonstrations of usefulness, it is accepted as one of the theories of science. This distinction between hypothesis and theory is not hypercritical; it is not always maintained, but it would serve a useful purpose if it were.

All enterprise, all originality existed first as hypotheses in the minds of men, and played a necessary part at some stage of all accomplishments.

Deduction. The process of thought just outlined, from the inner mental concepts, laws, and theories outward to the future, to experiments to be tried, is called deduction.

Probability. We have knowledge of past events and beliefs, but not knowledge concerning future events. Our laws summarize

our knowledge, our theories summarize our beliefs. On the basis, sometimes of our laws, sometimes of our theories, we strive to foretell what will probably happen under given conditions in the future. We are practically certain that days and nights will continue to alternate, but we seldom feel much certainty regarding the weather, and if we toss up a coin we are exactly evenly divided in our opinion as to whether it will come down heads or tails. When the event depends on chance, as in the last instance, we can calculate the chances and express them numerically; when incompletely understood connections, causal connections, exist, we cannot.

Comparison of Laws and Theories. Laws codify established facts, they are history; theories contain the possibilities of the future. Theories may be considered as knowledge in a state of flux, the mother liquor out of which there crystallizes now and then a clean-cut, precious new fact. We cannot say that one is more useful than the other, both may be fertile in suggestion, both are needed for progress.

The Scientific Method. To sum up, the scientific method consists, first, in experiment and observation. This must be followed by induction, and this by deduction, and this by experiment and observation again. The great advances of science are due to this systematic combination of experiment and right thought. Omit any part, either experiment or right thought, and we have dogma, bald assertions which have no standing in science.*

* For more extended treatment of the topics in this chapter and the next, and many interesting considerations not here included, the reader is referred to: "The Principles of Science," by Jevons; "The Grammar of Science," by Karl Pearson; "The Common Sense of the Exact Sciences," by W. K. Clifford; "Analysis of the Sensations," by E. Mach; "Natur Philosophie," by W. Ostwald; "Prinzipien der Chemie," by W. Ostwald.

CHAPTER III

FUNDAMENTAL DEFINITIONS

TURNING our attention outward, with the purpose to investigate the external universe, we are forced at once to make use of such terms as space, time, energy, mass, and weight. It is certainly important that we should know what we mean by these words. Philosophers have given much thought to their meaning, while scientists have given too little, and so the results obtained by philosophers sometimes cause surprise, even irritation, if preconceived opinions are too rudely shaken. We do not like to have it brought home to us how little we really know. Sometimes the views thus opened are called novel, radical, and subversive. They are none of these things. It is true conservatism to wish to know where we stand before we endeavor to advance. In our all-embracing haste, we are in danger of forgetting what was well known to our fathers and our grandfathers.

Properties or Attributes. All our knowledge of the external universe is obtained through our senses and consists then of sense impressions. Whatever produces an impression on our senses we call a property or attribute.

Object. The apparent source of a group of properties or attributes we call an object.

Space. We recognize differences in position. One position is above or below, in front of or behind, to the right or left of, north, south, east, or west of another. We can describe no position except by giving its relation to some other position. Our knowledge of positions is then exclusively relative, and it is exactly this observed relativity of position which gives us our idea that space exists.

If it exists it is a thing; we cannot think of a thing except as occupying space, and thinking of space as occupying space does not get us far along. A thing must have properties, attributes, otherwise we could know nothing of it. The only attribute of space we know is extension, dimensions. But these words mean relations between positions, *i.e.*, space. To say space is extension is saying space is space, and our progress remains imperceptible. Again, a thing has limits,

but we cannot think of space as limited. It must reach to infinity, and we cannot think of infinity. On the other hand, we cannot think of a space so small it cannot be further divided. It must be infinitely divisible, but we cannot picture to ourselves anything infinitely small. Space then is in fact incomprehensible, and yet we know it exists and what we intend to convey when we speak of it.*

Dimensions. Space has three dimensions. Why it does not have four or more we do not know, and speculations regarding the "fourth dimension" have remained unprofitable. Measurements in one dimension give us distances, in two dimensions, areas, and in three, volumes.†

Time. We observe sequences of events. One event happens after another or before another, and on such observations we base our idea of time. If time exists outside ourselves, it must make impressions on our senses. But we are at a loss to state what attributes it has which we perceive. Yet, if it has no attributes, it is nothing objective, and must exist solely in our minds, subjectively. This is a dilemma as uncompromising as the questions regarding space. We must conclude that time also is in fact incomprehensible, although we are all convinced of the reality and the existence, somewhere, of this abstraction, and we know what we mean by the word time.‡

Being based on sequences of events, on relations between events, time, like space, is relative.§

* See Herbert Spencer, "First Principles."

† The meter is our unit of distance, and was intended to be one ten-millionth of the quadrant of the earth's circumference drawn through Paris and the two poles. A slight error was made in the original measurements and our meter is too short by 0.02 mm. Therefore it is empirical, just as the yard is empirical, and it is, in fact, the distance between two marks on a platinum iridium rod preserved at the International Bureau of Weights and Measures at Sèvres near Paris. Another much used unit of distance is the centimeter, one one-hundredth of the above length.

The liter is the unit of volume. It is the volume occupied by that quantity of water at 4° C. which in vacuo will balance the standard kilogram preserved at the International Bureau. The customary definition, a cubic decimeter, is not accurate. For such readers as are not familiar with the metric system, a table is included in the appendix.

‡ See Herbert Spencer, "First Principles."

§ Our units of time have come down to us from the Babylonians. They divided the day into twenty-four parasangs or hours. Besides the decimal system, counting by tens, they had also a sexagesimal system of notation, counting by sixties. Thus it happens that our hour is divided into sixty minutes and our minutes into sixty seconds.

Motion, Velocity. When an object occupies a sequence of different positions in a sequence of time, we say it is in motion. The distance covered, divided by the time required for covering it, we call the velocity of the object.

Acceleration. Velocity as so defined may be increasing as time elapses; this increase in rate we call acceleration.

Inertia. An object in motion is capable of doing some work; we say it possesses a form of energy. When it does work, it loses a corresponding quantity of motion. An object at rest requires that work be done upon it to set it in motion; we say it possesses inertia.

Motion is Relative. Motion and rest are merely relative terms, referring generally to contiguous objects. We know of no object at rest. All objects on the earth's surface are revolving about the earth's axis, and with the earth about the sun, and with the sun toward the constellation of Hercules. We do not know the absolute velocity of anything.

Relativity Principle. It has been recognized for years by careful thinkers that the measures of science are all relative and that *absolute* measures are beyond our ability. This old friend has reappeared recently, masquerading as a novelty under the title of the "Relativity Principle" and has caused a species of consternation in some quarters; an appropriate illustration of the remarks in the first paragraph of this chapter. There is nothing new about the underlying principle, but some of the recent demonstrations are both novel and interesting.

Experiments lead us to state that the velocity of light is 300 000 kilometers a second. Michelson and Morley and others have determined the velocity of light in the direction in which the earth is moving and again at right angles to this direction, by methods which would surely have detected the influence of the earth's motion if it had existed. No such influence was observed. The velocity is always the same, relative to the observer, however measured.

Is the velocity of light influenced by the velocity with which the source of light may be moving? Suppose a star is approaching us at the rate of 10 000 kilometers a second; will the light come toward us at the rate of 310 000 kilometers a second? Suppose it is moving away at the same rate; will its light come to us at the rate of 290 000 kilometers a second?

Experiments always give a velocity of 300 000 kilometers, relative to the observer, independent of the direction and velocity of the

source. A brief description of one such experiment may be of interest. The sun is revolving about its axis at such a rate that a point on its equator moves nearly 2 kilometers a second. Tolman* compared the velocities of light from the approaching part and from the receding part in such a way that a difference in velocity would surely have produced interference phenomena. No such phenomena were observed; therefore the velocities are the same, relative to the observer.

This fact leads to a series of inconceivable conclusions. We receive light from a star moving away from us at the rate of 10 000 kilometers a second and find its velocity here to be 300 000 kilometers a second. We feel that an observer on that star, measuring the velocity of that light, would find a velocity of 310 000 kilometers a second. The star describes an orbit and presently is approaching us at the rate of 10 000 kilometers a second, and again we find the light from that star is moving with a velocity of 300 000 kilometers a second. We feel that the same observer on the same star, repeating his observation, should now find a velocity of 290 000 kilometers a second. This is absurd. We cannot assume that a star takes cognizance of its motion relative to the earth and emits light with a varying and appropriate velocity. It must be emitted at the same velocity wherever that star is in its orbit. An observer on that star must always get the same result that we do. We send him a signal flash as his world is moving away from us. It leaves us with a velocity of 300 000 kilometers a second. He measures its velocity as it reaches him and finds it is moving, relative to him, 300 000 kilometers a second; though in order to do this it must be moving at the rate of 310 000 kilometers a second relative to us. He returns the signal with a velocity of 300 000 kilometers a second relative to himself, which ought to be 290 000 kilometers a second relative to us. But when we receive it, it seems to be going at the rate of 300 000 kilometers a second. It is inconceivable that one and the same light should have two different velocities at the same time.

The observer on the receding star, measuring our signal, will obtain the value 300 000 kilometers a second instead of 290 000 kilometers if his second is longer than ours. But then, by the same reasoning, his second should be shorter than ours when his star is approaching us. This idea of compressed seconds or stretched seconds, that simultaneous seconds are of different lengths on different celestial bodies, is no more conceivable than the first conclusion.

* R. C. Tolman, *Physical Review*, 31, 26–40 (1910).

Our observer would obtain the same value that we obtain, even though his time were the same, if his kilometers were first shorter, then longer. That the distance between two points alters itself, now contracting, now expanding, is likewise inconceivable.

We cannot avoid the conclusion that we have no "absolute" measures of time nor distance. Time and distance enter into every other unit of measurement, therefore all our units are merely relative to the observer.

By this route scientists are painfully reaching the same conclusion reached by philosophers many years ago, that "absolute" measures are impossible for us, and we are confined by the nature of our intellects to relative measures.

Energy. We have used the word energy, and this stands, without doubt, for the most comprehensive and fundamental concept of all objective sciences. If we see an object, it is through the medium of radiant energy, light, which acts on the retina; if we hear, it is through the medium of kinetic energy acting on our ear drums; if we smell or taste, the sensation may be traced to chemical energy producing effects at the sense endings; if we feel, it is kinetic energy again, for we impart motion to our fingers, and feeling consists in compressions or displacements of nerve endings in our fingers. Energy is then the name we give to whatsoever produces an effect on our senses.

It may be permissible to cite a well-worn illustration. Imagine yourself moving along rapidly in utter darkness, and imagine a stick following close behind you at the same rate. You have no knowledge whatever of the presence of the stick. If you stop suddenly, you will immediately become conscious of its existence. What calls the stick to your attention is solely the difference in rate of motion, *i.e.*, kinetic energy. Even then you know nothing of the total kinetic energy of the stick; it is merely relative.

Definition of Energy. Since all our knowledge of the objective universe comes to us through our senses, and since a form of energy is the only thing that can affect our senses, we may define energy as *whatever leads us to believe that something exists outside our own consciousness*, that there is a universe in which we live. This is to be preferred to the more usual definition that energy is the ability to do work.

Number of Properties. Properties or attributes are then manifestations of energy, and all we know is a number of properties and

relations between properties. We have learned to observe and describe many properties, but we have no reason to suppose we have exhausted the list even for one simplest object.*

Substance. Properties are of different degrees of importance, depending upon the purpose of our study. In chemistry, we are interested in the properties by virtue of which a substance is what it is, and we disregard accidental properties, such as position or size. Marble is calcium carbonate for us in our capacity as chemists, whether it be a small lump in the laboratory or a masterpiece by Praxiteles.

We abstract from an object those properties which make it what it is, and a group of properties so obtained is what we mean by the word substance.

Identity. One of the purposes of the science of chemistry is the establishment of identity or differences between samples of substances. It is not the only purpose, not even the most important purpose, but it is one of its uses, the finding out what a substance is, and, by analysis into simpler substances, what it contains. We measure only a few of the properties of each sample and, if these agree, we say their sources, the substances, are identical. We make use, subconsciously, of a great law here: When two sources agree in a number of their properties, they agree in all. This law is based on all experience.

Sometimes not enough properties are studied before the conclusion is reached that identity exists. For example, a neglect of some of the properties of nitrogen obtained from the air, as compared with nitrogen obtained from ammonium nitrite, prevented chemists from discovering argon and the other rare elements of the atmosphere until 1895. How many properties must be measured and compared before we declare two substances to be identical we do not know. Experience teaches us that comparatively few serve the purpose in most instances.

Processes. Sulphur burns, and as a result of the combustion we get a very different group of properties from that which we had originally. Water freezes, and another set of properties springs into evidence. Whenever we note a change in properties, what we actually observe is a transformation or redistribution of energy. These changes in properties are what we call processes.

* Read Voltaire's story, "Micromegas," for an amusing account of the impressions of an imaginary individual from another planet endowed with more senses than ourselves.

Physical Processes. Processes may be divided into two classes in such a way as to furnish a fairly useful, although not wholly satisfactory, distinction between physics and chemistry. As physical, we may include all processes which do not produce permanent change. Electrical energy passes through a wire and the wire is thereby heated and becomes possessed of new properties, such as an ability to deflect the needle of a compass, but it is not permanently changed. When the current ceases to pass, we have the original wire unaltered.

Chemical Processes. Processes causing permanent changes may be classed as chemical. Electrical energy passing through a solution electrolyzes the solution, and new substances appear at the electrodes. These new substances do not disappear when the current ceases.

Physicochemical Processes. In every branch of chemistry we make use of the processes of distillation, melting, and freezing, and crystallization. They belong in both chemistry and physics and may be called physicochemical. It is quite impossible to draw a hard and fast line between the sciences. The so-called physicochemical constants of a substance, the boiling point, freezing point and specific gravity, are determined many more times by chemists in their work than by physicists in theirs.

Classification of Energies. We have no means of knowing how many forms of energy there are; there may be an infinite number, or in reality only one, but we can classify all manifestations which we have studied under relatively few heads. Any given process may be considered as a manifestation of one or more of the following eight forms of energy: kinetic, linear, surface, volume, heat, electrical, chemical, radiant. This list serves our purpose well. But other classifications are possible and no one must be considered as necessary to the exclusion of others. One classification is more convenient for one purpose than another. For instance, for some purposes it may be more convenient to include the first four forms of this list under the one name " mechanical " and then subdivide this into kinetic and potential.*

Division of the Subject into Topics. One advantage of some such classification is that it enables us to systematize our study. For

* Electrical energy, light, and radiant heat are essentially the same. This is deeply interesting, but it remains convenient to present our knowledge under the subdivisions as indicated. Even if we finally demonstrate all energies are one in kind, it will remain convenient to subdivide the subject.

instance, the processes in which mechanical energies are converted into each other constitute the subject mechanics. Those involving the transformation of electrical into chemical energy, and the converse, fall under the title, electrochemistry. Transformations of radiant energy into chemical, and the converse, are the subject matter of actinochemistry, also called photochemistry. (Photography is but a small, though interesting, subdivision of this topic.) The processes in which heat is converted to chemical energy, and the converse, are grouped under the name thermochemistry, and those in which heat is converted to mechanical energy are grouped together as thermodynamics.

There is nothing hard and fast about this subdivision into topics either. One merges into the other and it is quite impossible to treat of one to the exclusion of all others. Thermochemistry and thermodynamics are incorrigible interlopers intruding into nearly every cranny of science.

Division of Energies into Factors. W. J. M. Rankine (1820–1872)* first suggested that it was possible to consider a quantity of energy as divided into factors such that their product equaled the whole of the energy; and that these factors might be so chosen that one, called the intensity factor, determines whether a transference of energy will occur or not, and in what direction; and another, called the quantity or capacity factor, determines to what extent the change takes place.

Here again such division is not a necessity inherent in the nature of energy, but it is a convenience. If, in experimental work, there are several variable factors, we strive to hold all but one constant and study that, then the next, and so on. A problem, insoluble as a whole, thus dissected, often becomes easy. Considering energies as products of separate factors enables us to divide many problems into parts and solve them piecemeal.

In some cases we cannot carry out this division into factors advantageously. For example, we have not thought of factors for radiant energy which aid us perceptibly with our problems. Moreover, it may be convenient for some problem to consider an energy as divided into two factors, and for another problem as otherwise divided. For instance, for one purpose it is convenient to consider heat energy as equal to heat capacity times temperature, and for another purpose to consider heat energy as entropy times tempera-

* Dates after names give years of birth and of death.

ture. Again, there is no necessity that there shall always be two factors and no more. For instance, kinetic energy may be considered as $\frac{1}{2} \times m \times v \times v$, four factors. In such case, however, one or more factors partake of the nature of intensity factors, determining whether transferences will occur, and the others partake of the nature of capacity factors, determining the extent of the transference. There may be a difference of opinion as to just what factors are preferable, but there can hardly be a difference of opinion as to the advantage derived when we can so render a complex problem simpler.

Table of Energies and Their Factors. The following is a table containing one convenient classification of energies we are competent to study and their factors.

	Quantity Factor.	Intensity Factor.
Kinetic	Mass	Square of the velocity
Linear	Distance	Force
Surface	Surface area	Surface tension
Volume	Volume	Pressure
Heat	Calories*	Temperature
Electrical	Coulombs	Volts
Chemical	Valence	Affinity
Radiant		

* Too much stress must not be laid upon the particular subdivisions given in the above table. In some problems rigid adherence to calories as the quantity factor leads us to contradictions and inconceivabilities. We must remember that our classifications and definitions are relative, artificial, capable of alteration and improvement, well adapted for some purposes, but not necessarily for all which may arise. We must be willing to use those best adapted and must not try to force one favorite method into every problem. As well might a carpenter try to build a house with one tool.

Law of the Conservation of Energy. As a result of countless experiments, it has been found that no matter what process we study, if a quantity of one form of energy disappears, an exactly equivalent quantity of some other form appears. We have never succeeded in creating or destroying any energy, nor have we ever observed any process in which such creation or destruction occurred. All these experiences have been combined in one statement, known as the law of the conservation of energy, the most important and fundamental law of all science. It is often stated as follows: Energy can neither be created nor destroyed, or: The total energy of the universe is a constant.

Objections to Form of Statement. These sentences are open to objections, stating as fact more than we really know to be fact. We do not know how much energy there is in the universe. We do not even know how many different kinds of energy there are. We do not know what conditions prevail on other planets or fixed stars, or beyond the fixed stars, yet within that broad term we use so glibly, the " universe." We ought to append to these statements a modifying phrase such as, " as far as our experiences have taught us." A convenient form in which to state the law, and one free from the above objections, is: The total energy of an isolated system remains constant. By " system " we mean any substance or set of substances we are studying, as distinguished from its surroundings.

This law marks a limit of our finite minds, and it is interesting to realize that we have not the suggestion of an hypothesis to explain it. It was first clearly stated by Robert Mayer in 1842, but without doubt was silently recognized by others before him; probably by Sadi Carnot and possibly by Lavoisier. Perhaps even it was taken as such a matter of course that it was not supposed to require specific statement.

The First Law of Thermodynamics. That portion of the great law which applies to processes involving transferences of heat, or transformations of heat into mechanical energy, and the converse, is called the first law of thermodynamics.

Perpetual Motion. Perpetual motion is of course possible, as is stated in the first law of motion, " Motion continues in a straight line undiminished in velocity unless acted upon by some external force." A top set spinning under conditions where there is no friction will never cease to spin. These conditions are very nearly realized in the motions of the planets and stars. The statement that energy cannot be destroyed asserts this possibility.

But by " perpetual motion " is generally meant a machine which will do work and keep going though energy equivalent to the work done is not given to it. Many attempts have been made to construct such a machine. They have all failed. The statement that energy cannot be created denies the possibility of such a machine.

Total Energy. We have no means of knowing what is the total energy in any one system, for all our measurements are relative. For example, we cannot even measure the absolute kinetic energy of a single object, for, as we have seen, we know nothing of absolute velocities.

Available Energy. When a process occurs we can measure the energy which is transferred or transformed. We may call this available energy. Subtract this and what is left we may call unavailable energy.

Free Energy. We have learned by experience that all other forms of energy may be converted without loss to heat, but the converse is not true. Heat cannot be converted completely to other forms except under well-defined conditions. That fraction of the heat which we can convert to another form we call free energy. Subtract the free energy and what is left may be called bound energy.

The first distinction is between energy which we can measure and that which we cannot measure. The second distinction is between the energy we can make do useful work and that which we cannot.

Reversible Processes. Imagine a pendulum swinging in vacuo on a knife edge without friction. Starting from its highest position to the right, potential energy is converted completely to kinetic energy when it reaches its lowest point, and this in turn is converted completely to potential energy when it reaches its highest point on the left. Arrest the pendulum here. A process has occurred. Release the pendulum and it will swing back to exactly its original position, and no energy has been gained or lost. The system is capable of repeating the performance as often as we please. This is typical of what we mean by a reversible process.

If, in a process, any of the available energy is converted to heat, this heat will not convert itself back completely to the original form, and the process is accompanied by a loss of free energy. This is characteristic of all processes with which we actually have to deal; they are accompanied by a loss of free energy, for frictionless machines may be imagined but we have not constructed any. A general leveling is going on and we are tending to the condition of an extinct planet, like our satellite, the moon, where the happenings are few.

The Second Law of Thermodynamics. The statement that there is a loss of free energy in all but reversible processes, and that a reversible process cannot be made to do work unless free energy is given to it, which means that there is a loss of free energy somewhere, is what is called the second law of thermodynamics.

Matter. We observe that portions of space differ from the rest in being, as we call it, occupied. Whatever occupies space we call an object. An object resists an effort to lift it and falls when released. We say it has weight. Whenever we meet these two attributes, ability

to occupy space and having weight, we say matter is present. The word matter should then be understood as an abbreviation for the long phrase, "the attribute having weight accompanied by the attribute ability to occupy space."

Carriers of Energy. It is a peculiarity and a limitation of the human intellect that it has difficulty in conceiving of attributes or properties by themselves, and, perceiving some property, at once hypothecates something as a carrier of the property. The hypothetical carrier of the attributes, having weight and ability to occupy space, is what many mean when they use the word matter.

Study an object as we will, we never learn anything but more and more of its properties; never can we get at that mysterious something imagined as present and as the carrier of the properties. We can imagine an object as deprived of one property after the other until we have removed every known property, and what have we left? Imagine any object you will, deprived of weight, and then deprived of the power to resist the passage of anything through it, and what is left? We do not know at all, and yet that mysterious carrier must remain, since we removed only properties, which perhaps were considered as changeable, "immaterial," evanescent ghosts, more or less temporarily attached to the real thing. But we must confess a complete inability to say anything definite about the "real thing." It is totally unknown and indescribable.

There is no subject in all science where misunderstandings are more pronounced or harder to clear up than here. The trouble is that so many consider matter as axiomatic, requiring no definition, the fundamental fact from which to start. For them matter is the only thing that matters. Those so hardy, and they are many and increasing in numbers, as to inquire into the question in a sincere effort to obtain a definition free from objection, are sometimes called dreamers and their adversaries claim a monopoly of "good hard sense." The fact is the positions are precisely the reverse. The "dreamers" are unwilling either to assert or deny the existence of a something totally unknown and indescribable, and those who assert that that and energy are the only things that really exist are in truth the dreamers. They may be right, but their confidence is unwarranted.

Weight. We have defined the word matter as an abbreviation for "having weight and occupying space." Weight is the measure of the attraction of gravitation between two bodies. Newton's law of gravitation states that this attraction varies inversely as the square

of the distance between the two centers of gravity and directly as their masses. If m_1 is the mass of an object, m_2 the mass of the earth, and d the distance between their centers of gravity, then the weight $w = \frac{m_1 \times m_2}{d^2}$. A given object weighs less at the equator than at the poles. The earth is flattened at the poles; therefore, at the poles the value d is less than at the equator. The object would weigh less on the surface of the moon, for the mass of the moon is less than that of the earth, and more on the surface of Jupiter, for Jupiter's mass is greater than that of the earth. Weight then is variable, and, on the surface of the earth, a function of the latitude in which the weighing is done.

The Acceleration of Gravity. A body, falling freely from a position of rest in latitude 45° at the end of one second will be falling 980.6 cm. per second. If it has an initial velocity, at the end of one second it will be falling 980 6 cm. per second faster. This is called the acceleration of gravity. At the equator its value is 978.1; at the poles 983.2; at Washington, D. C., 980.07; at Cambridge, Mass., 980.59; and so on. It is not constant except for a given latitude.

Mass. An object cannot be imagined as altering when it is moved from place to place, though its weight does. That property which does not alter and which is represented in the above equation as m_1 or m_2 is what we mean by mass. We measure it in terms of weight. Weights are always proportional to the masses, and so, if all weighings are made at one place, the numerical values of weights found may be substituted for masses without error. But the two terms are clearly not synonymous.

The Conservation of Mass. This property, mass, is peculiar. All other properties we can alter or cause to disappear, but not so mass. It persists as such in unaltered quantity, no matter what process we study. This is the generalization extracted from all the countless quantitative experiments ever made. It is known as the law of the conservation of mass, and was first announced by A. L. Lavoisier (1743–1794) in 1774. It may be stated as follows: Mass can neither be created nor destroyed, or: The total mass of the universe is a constant. These statements are open to the same objections as those brought against the statements of the law of the conservation of energy. They say more than we really know, although they are based upon an enormous number of experiments. The same qualifying phrase should be added, "as far as our experience has taught us." (M14)

Landolt's Experiments. Landolt has subjected this statement to the most rigid experimental investigation the resources of modern scientists and instrument makers would permit, and concludes that in the thirty or more chemical reactions he studied any gain or loss in weight is certainly less than one ten-millionth part of the total weight.*

Length of Year Proof. One of the best illustrations of this generalization is obtained from astronomical measurements. The length of the year depends upon the mass of the earth and that of the sun, and this time interval has not changed since measurements were made, in spite of the gigantic chemical processes which are occurring on the sun, not to mention everything that happens on this earth. No hypothesis has been advanced as a plausible explanation of the remarkable facts comprised in this law.

Gram. The unit of mass (weight) is the gram. It was intended to be the mass (weight) of one cm^3 of water at its temperature of maximum density, 4° C. But minute errors were made in the original measurements, and so it is empirical, one one-thousandth of the mass of the standard kilogram of platinum iridium alloy preserved at the International Bureau.

Dyne. The dyne is the unit of force and is the force which, acting for unit of time (one second), upon unit of mass (one gram), will impart to it unit of velocity; *i.e.*, will cause a unit of mass to be moving, at the end of the first second, at the rate of one centimeter per second.

Work. When a force has acted through a distance we say work has been done. This appears in the table of energies (p. 25) as linear

* Landolt reports the result of his experiments, which extended over fifteen years, in *Sitzungsberichte d. K. Pr. Akad. d. Wissenschaften*, **16**, 354 (1908). An excellent summary of this report may be found in *Journal de Chimie physique*, **6**, 625–27, 1908. He noted a number of hitherto unsuspected sources of error. The heat of the reaction evaporated a little of the film of moisture normally present on the outside of glass vessels. A glass vessel having an external area of about 380 square centimeters, enclosed in a desiccator over sulphuric acid for 48 hours, lost 0.121 milligram, and regained its original weight only after two days in the air. The heat due to the reaction expands the glass, and it requires about two weeks to return to its original volume. A vessel occupying about 234 cubic centimeters was raised 40°, and one day later the increase in volume was found to be 0.028 cubic centimeter. Only after 14 to 18 days did the vessel resume its original volume.

A student should read such reports as this in the original to learn what truly careful work is like, and what an immense amount of labor lies hidden behind the concise statements of science.

energy, of which distance is the capacity factor and force the intensity factor.

Erg. The erg is the unit of work and is the quantity of energy which has manifested itself when unit of mass has been moved through one centimeter against a force of one dyne, regardless of the time consumed in the process.

Gram-Centimeter. The gram-centimeter is the work done when one gram is lifted one centimeter against the force of gravitation. One gram-centimeter equals 980.6 ergs in latitude 45°. The proportionality factor by which to convert gram-centimeters to ergs at another place is the acceleration of gravitation at that place.

The difference in the concepts for which the words energy, force, and work stand may be remembered by the following examples. A coiled watch spring held by a catch contains energy and exerts a force on the catch. Release it and energy becomes manifest and does mechanical work, which is measured in ergs, gram-centimeters, or a similar unit. All work is energy, but all energy is not work. A storage battery contains energy, and when the poles are joined by a wire, energy becomes manifest as electrical energy and heat. We cannot call this work except by analogy and by calculation, using a proportionality factor. Energy is the general term comprehending all others; work is a particular variety of which force may be considered as the intensity factor.

Comparative Units. Density is the mass per unit volume. Specific density is the ratio between the mass of any volume of one substance, and the mass of an equal volume of some other substance which has been taken as a standard.

Specific gravity is the ratio between the weight of any volume of one substance, and the weight of an equal volume of some other substance which has been taken as a standard. Density, specific density, and specific gravity become identical if a substance with the density one be taken as the standard in comparisons.

Specific volume is the ratio between the volume occupied by any weight of one substance and the volume occupied by an equal weight of some other substance which has been taken as a standard. If a substance, unit weight of which occupies unit volume, has been taken as a standard, the specific volume is the volume occupied by unit weight.

The term "specific" always implies a comparison and "specific" values are ratios.

Conditions of Aggregation. It is convenient to classify substances according to what we call their conditions of aggregation, or, more briefly, states. These are, solid, liquid, and gaseous; and to these is frequently added a fourth, for reasons which will develop later, the condition of being in solution.

Gas. A gas is a substance which fills completely a containing vessel of whatever size. It is a substance having neither definite volume nor definite shape.

Gas Laws. We have succeeded in discovering simpler and more comprehensive generalizations for gases than for any other condition of aggregation. It is probably safe to assume a knowledge of the gas laws, but they are so fundamental in so many of our future considerations it may be well to review them summarily.

Boyle's Law. In 1662 Robert Boyle (1627–1691) discovered the fact that if the temperature of a gas remains constant, its volume varies inversely as the pressure upon it. This is most conveniently expressed in the proportion,

$v : v' = p' : p$; or in the equation, $pv = p'v'$, or $pv =$ a constant.*

Isotherm. The law may be expressed graphically by plotting pairs of values for p and v on a coördinate system; values for p on the abscissa and corresponding values for v on the ordinate. We thus obtain a curve as shown in Fig. 1. It is a right angle hyperbola of such a form that $p = 0$, when $v =$ infinity, or $v = 0$ when $p =$ infinity. As this curve is obtained while the temperature is held constant, it is called an isotherm.

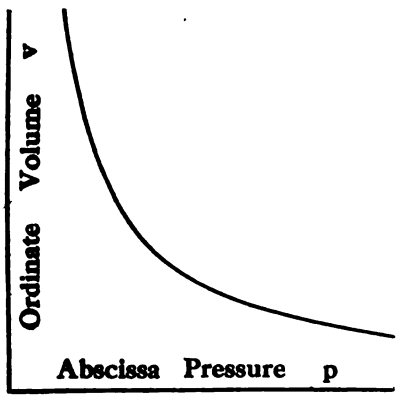


Fig. 1.

Gay-Lussac's Law. In 1801, J. L. Gay-Lussac (1778–1850) observed and stated that all gases expand at the same rate and contract at the same rate when their temperature is altered while the pressure is held constant.†

* This law was discovered, probably independently, by E. Mariotte (1620?–1684) in 1679, but there is no question but that the priority belongs to Boyle.

† This is also known as Charles' Law. Charles discovered it a few years before Gay-Lussac but did not publish his results. Amonton knew the law in 1702, or

Isobar. In a coördinate system, lay off temperatures on the abscissa and volumes on the ordinate. As the pressure is held constant, the curve (straight line) so obtained is called an isobar. One liter of a gas at the temperature of melting ice becomes 1.367 liters at the temperature of boiling water. The expansion of gases is very nearly, but not exactly, a linear function of the temperature, and so a line joining the points thus determined is very nearly but not exactly a straight line, as shown in Fig. 2.

Let the temperature at which ice melts be denoted by 0°, and the temperature at which water boils (when the pressure is 760 mm.) be

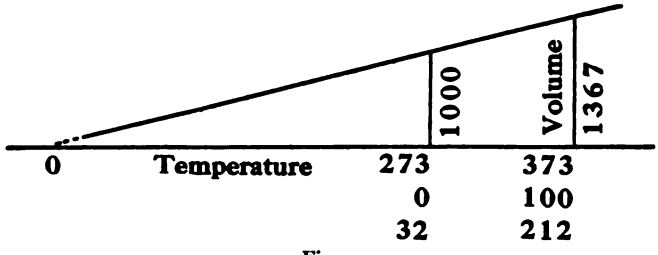


Fig. 2.

denoted by 100°. Divide the interval into 100 equal parts, and in this way we obtain the centigrade or Celsius temperature scale.*

The Absolute Zero. The isobar continues as a nearly straight line below 0° centigrade as far as it has been measured. Produced beyond the experimentally observed points by extrapolation, as shown by the dotted line in the diagram, it cuts the horizontal at a distance of 273 centigrade scale units below 0°. This point, corresponding, according to the diagram, to no volume (or no pressure), has never been reached. It is hypothetical. We call it the absolute zero.

nearly one hundred years earlier, so that strict regard for priority would oblige us to rename it Amonton's law. Usage is about evenly divided between "Charles" and "Gay-Lussac." Dalton also discovered the law shortly before Gay-Lussac.

* The Fahrenheit scale is obtained by putting the temperature of melting ice at 32° and the temperature of boiling water at 212°. This divides the interval into 180 equal parts.

The Reaumur scale is obtained by putting the temperature of melting ice equal to 0° and the temperature of boiling water at 80°, and the interval is divided into 80 equal parts.

The lengths of the centigrade or Celsius degrees, are to the lengths of the Reaumur degrees, are to the lengths of the Fahrenheit degrees, as 5 : 4 : 9, and this easily remembered proportion enables us to convert temperatures from any one scale into any other. In all science, we use exclusively the centigrade scale.

It is the origin of the very useful " absolute " scale, on which there are no minus signs. Temperatures on this absolute scale are, by convention, always indicated by T, while temperatures on the centigrade scale are indicated by t.

Formulation of Gay-Lussac's Law. With the assistance of this absolute scale, we may formulate Gay-Lussac's law conveniently. We may say, the pressure remaining constant, the volume of a gas varies directly as its absolute temperature, or $v : v_1 = T : T_1$.*

The Third Law. There are three conditions which we may vary: pressure, temperature, and volume. We have considered the interdependence of the two remaining variables when each of the first two are held constant. There remains to consider the relation between pressure and temperature when the third, the volume, is held constant.

It follows as a necessary corollary of the first two laws that when the volume is held constant the pressures are directly proportional to the absolute temperatures; or, $p : p_1 = T : T_1$.

Isochor. Plotting corresponding values of p and T on abscissa and ordinate, we obtain a curve (straight line), called the isochor, because the volume is held constant.

Combining the Laws to one Expression. We may combine these three laws into one simple expression as follows: Let p_0, v_0 and T_0 represent the initial conditions and p_1, v_1 and T_1 the final conditions of a volume of a gas. Change p_0 to p_1 while the temperature is held constant. In this way we obtain what we may call an intermediate volume, which we shall denote as v_x. Applying Boyle's law, we have

$$v_0 : v_x = p_1 : p_0, \text{ or } v_x = \frac{p_0 v_0}{p_1}.$$

Now change the temperature from T_0 to T_1, while we hold the pressure constant at p_1. Applying Gay-Lussac's law, we have $v_x : v_1 = T_0 : T_1$. Substituting the value for v_x and multiplying out the proportion, we obtain, $v_1 T_0 = \frac{T_1 p_0 v_0}{p_1}$, and transposing, we get $p_1 v_1 = p_0 v_0 \frac{T_1}{T_0}$, the most general expression for all the relations.

Standard Conditions. We adopt what we call standard or normal conditions, the temperature 0° centigrade, and the pressure 760 mm. of mercury, which is the average atmospheric pressure at the sea level.

* A more common but less good formulation of the law is:
$v_1 = v_0 (1 + \frac{1}{273} t) = v_0 (1 + 0.003\,67\, t)$, or $v_1 = v_0 (1 + \alpha t)$. Where v_0 equals the volume at 0°.

The Gas Constant. Zero centigrade is 273 on the absolute scale and we may insert this in our equation, and write it $p_1v_1 = T_1 \frac{p_0v_0}{273}$.

If, at the same time, we have the standard pressure ($p_0 = 760$ mm.), two of the three variables have definite numerical values and the third, v_0, must also. All these values, p_0, v_0 and T_0 being constant, the whole term is a constant. We may then, for this term, insert a symbol, R, called the gas constant. We thus reach the final and most general expression of all the gas laws, $pv = RT$. In words, this states that the product of the pressure and the volume is proportional to the absolute temperature times a constant.

The Gas Laws are Limiting Laws. These laws as thus stated are limiting laws; they do not formulate accurately the behavior of any known gas. An imaginary gas whose behavior would exactly correspond to our formula we speak of as an ideal gas. Gases correspond in their behavior to this formulation best at high temperatures and low pressures. They are too compressible when near their points of condensation, and are not compressible enough when the pressures are high.*

The behavior of gases thus enables us to establish temperature scales and to measure temperatures, the intensity factor of heat energy.

Thermometers. Owing to the fact that the expansions of mercury and of hydrogen are not exactly linear functions of the temperature, though nearly so, there is a difference between the readings with a mercury thermometer and a hydrogen thermometer. This may be neglected in all but the most accurate work.

Small Calorie. The unit of quantity of heat is the small calorie, also called the gram calorie, written cal., and it is the amount of heat required to raise one gram of water from 15° to 16°. It is necessary to state the exact temperature interval, because the specific heat of water is different at different temperatures.

Large Calorie. The large calorie, also called the kilogram calorie, written Cal., is the amount of heat required to raise one kilogram of water from 15° to 16°. 1 Cal. = 1000. cal.

Specific Heat. The specific heat of a substance is the ratio between the number of calories required to raise a given weight of the

* It is necessary that a student of physical chemistry should be able to do problems involving the application of the gas laws readily. A description of the method of calculating such problems, and examples, may be found in the appendix.

substance through a given temperature interval, and the number of calories required to raise the same weight of the standard substance through the same temperature interval. Water is almost always the standard substance and so the specific heat of a substance is the number of calories required to raise one gram one degree centigrade. But it must be remembered that the specific heat of a substance is different at different temperatures.

Heat Capacity. The heat capacity of a substance is obviously the specific heat multiplied by the quantity of that substance. The heat capacity of a system is the sum of the heat capacities of all the substances in the system.

Mechanical Equivalent of Heat. It has been found by experiment that one calorie is equivalent to 42 660 gram-centimeters of work.* This is called the mechanical equivalent of heat.

Liquid. A liquid is a substance which will fill completely the lower part of a containing vessel. It is a substance having a definite volume but no definite shape. We have no such broad generalizations for liquids as the gas laws, and considerations of details are reserved for later chapters.

Solid. A solid is a substance having both definite volume and shape. Solids may be crystalline or amorphous. If, to this definition, we add that a solid has a definite melting point, then amorphous solids must be considered as very viscous liquids. One classification is useful in some discussions, the other in others.

Solution. A solution is a mixture of substances chemically and physically homogeneous throughout, the proportions of whose components may be altered continuously without producing an abrupt change in any property of the solution. The full significance of this definition will appear later. It is at once evident that we may have solutions in each of the three conditions of aggregation; we may have gaseous, liquid, and solid solutions.

Solvent and Solute. When two substances form a solution it is customary to refer to that present in the larger quantity as the solvent, and to the other as the solute. But these are really interchangeable terms, and if, for example, we have a solution containing alcohol and water in equal volumes there is no criterion by which to determine which of these shall be called the solvent and which the solute.

* Many determinations have been made. This recent value we owe to Callendar and Barnes. *Phil. Trans.*, 199, 149 (1902).

The Principle of Continuity. Continuity is observable in almost all the phenomena of nature. The boundary lines between the conditions of aggregation are not fixed and definite, and under certain conditions one state merges into another. Above the critical temperature the change from gas to liquid may be made to occur and yet not be observable. Liquids of increasing viscosity may be selected from the very mobile, such as ether or carbon disulphide, through oils, molasses, putty, wax to glass, a substance commonly classed as a solid. But a glass rod, supported at the ends, will gradually bend, and this is "flowing"; the same phenomenon as the flowing of water down hill, only slower. Rocks "flow" under great pressure in the course of geologic ages. Thermometers are evacuated and the pressure of the atmosphere may cause the glass to flow and diminish the internal capacity. A thermometer, accurate to-day, may give readings which are too high a year from to-day, from this cause.

Melting Point. A lack of continuity worthy of notice is shown by crystalline solids. They invariably have definite melting points, above which they are liquids, below which they are solids.* Amorphous solids have no definite melting points, and this is the reason they may be considered as liquids of great viscosity.

Continuity in Solutions. Another instance of continuity is furnished by a series of solutions. At one extreme we have what we may call a true solution, such as copper sulphate dissolved in water. The solute has not the slightest tendency to separate out in time; on the contrary, if the solution is not homogeneous throughout to begin with, diffusion proceeds until it is. At the other extreme we have suspensions, as of sand in water, which separate rapidly. Between these extremes we have every conceivable gradation; extremely fine precipitates take an appreciable time to settle out; an emulsion of sufficiently fine oily globules may take hours, as, for instance, cream rising above milk; milk itself is an emulsion which will not separate in a long while; in colloidal solutions the particles may be seen and counted by ultramicroscopic methods, and yet colloidal solutions of metallic gold have been preserved for sixty years without separating out. It is hard, if not impossible, to draw a definite dividing line between true solutions and colloidal solutions on the one hand, or between colloidal solutions and suspensions or emulsions on the other.

Classifications are Artificial. This continuity in nature is constantly interfering with our efforts at classification and subdivision

* The existence of "liquid crystals" is not an exception to this statement.

of subjects; indeed we have already experienced the inconvenience several times. It forces us to realize that most of our classifications are artificial and not natural. The objective universe is one continuous whole without a beginning and without an end, so far as we know. When we begin its study we plunge into the middle of it, and are entirely free to strike out in any direction. We cannot tell beforehand which way is easy and which hard. The terms "elementary" and "advanced" convey false impressions, for the "elementary" subjects are merely those taken up first, and often are harder to master than are the "advanced" subjects, which are taken up later.

SECTION II

STOICHEIOMETRY

CHAPTER IV

UNIT QUANTITIES OF CHEMISTRY AND CHEMICAL NOTATION

Stoicheiometry. Beginning with this chapter and continuing through Chapter X we shall be dealing with efforts to answer the question, what are the ultimate constituents? This subject is called stoicheiometry, a word which, by derivation, means the measurement of the constituents.

The rules of right thought must be followed, and the facts, obtained by experiment and observation, which form the starting point of each line of reasoning, must be presented before the reasoning is begun. It is therefore necessary to state briefly a number of familiar generalizations and definitions; but a rapid review is seldom unprofitable.

Chemical Compound. When substances interact with the permanent loss of some properties and appearance of new properties, we say a chemical compound has formed. We have learned by experience that most substances may be split up by suitable processes, called analytical, into simpler substances, and that beginning with these simpler substances, we may build up the original compounds again by methods called synthetical.

Elements. A comparatively small group of about eighty substances have thus far resisted all our efforts to analyze them into simpler substances. Having this property in common, they form a class by themselves, and we call them elements. Because, with our finite means and finite intelligence, we have not succeeded in splitting them is not sufficient justification for saying they cannot be split. Indeed, we know facts about the elements which incline us to believe that we could break them up if we had more energetic methods of analysis, and knew how to apply them.

If these substances are not elements in the original sense of the word, they nevertheless have so many "class" properties that we are justified in assuming they are of the same order of complexity.

We never can state exactly how many elements there are, for the list may be likened to an exclusive club. There are always a few substances about which we are in doubt as to whether they should be included or not. They have not, as yet, been sufficiently investigated.

Combining Weights. John Dalton (1766–1844) observed the facts and stated the generalization so well known to us as the law of definite and multiple proportions by weight.* He recognized that from the ratios obtained by analysis, a different numerical value could be picked out for each element, representing the parts by weight with which it enters into combination, and that no matter what the compound, the parts by weight of each element in it could be represented by the characteristic number belonging to that element, or some simple whole number multiple of that number. These characteristic numbers, most essential properties from the chemist's standpoint, are often called the combining weights of the elements. They are also called the stoicheiometrical constants.

The Law of Definite and Multiple Proportions by Weight. With the assistance of this term we may state the law, which is sometimes called the law of constant proportions by weight, as follows: The elements unite to form chemical compounds only in the proportions expressed by their combining weights, or simple whole number multiples thereof.

This law, as stated, contains a definition of chemical compound, and excludes all substances which do not contain their constituents in definite parts by weight from that category. It is entirely possible that when a substance goes into solution we have a manifestation of the same kind of energy as that manifested when elements unite to form chemical compounds. Too rigid adherence to particular definitions or classifications, however well established and time honored, is undesirable, for it sometimes leads to prejudices, a reluctance to accept facts or give particular views due consideration, and so retards

* The first facts and ideas appeared in Dalton's paper "On the Absorption of Gases by Water and other Liquids," read October 21, 1803, published in "Memoirs of the Literary and Philosophical Society," Manchester, second series, Vol. I. More complete descriptions are contained in his "New System of Chemical Philosophy," Vol. I, 1808.

the advance of science. The mind must be kept open and the judgment impartial at all costs.

A different wording of the law, admitting the possibility of the above suggestion, might be preferable. But any modification must still state the observed facts; they are past events, not capable of alteration.

The Law of Combining Volumes. Practically simultaneously with Dalton's discovery, Gay-Lussac announced the law which is no less valuable for the establishment of our chemical units and chemical notation than the law of definite and multiple proportions by weight, namely, the law of combining volumes. The facts are familiar. We may state the generalization as follows: If gases interact and form a gaseous product, the volumes of the reacting gases and the volumes of the gaseous products are to each other in very simple proportions, expressible by small whole numbers.

On these two laws we base the whole of our system of chemical units and chemical notation.

Historical. It is practically certain that Dalton, as a result of his study of Isaac Newton's works, conceived the atomic theory of chemistry in his own mind, without a shred of experimental evidence. He then proceeded by deduction, made surprisingly few experiments, found they corresponded to his preconceived ideas, and one of the most beautiful and useful classification systems ever evolved by the mind of man was fairly launched.

The way in which this system is now presented, with very few exceptions, is more logical. Experimental facts are described; from these the law is extracted; as a plausible explanation of the law the atomic theory is given. From this idea, the result of induction, deductions are made, and we have our atomic weights, formulæ, and equations.

No exception can be taken to this method as such, for it is typical of right thought. The only trouble with it is that it is too good. Beginners are almost infallibly convinced by it of the objective reality of atoms. They feel that some particularly expert scientist, somewhere, with exceptional microscopes, knives, and tweezers, has dissected all substances, and inspected, counted, and weighed single atoms. This confusion of fact with theory, particularly at the outset, is truly harmful. If permitted in so important an instance, it will always be more difficult to distinguish fact from theory, and that injures the faculty of right judgment. Of course a readjustment is

effected later, and a careful thinker uses the atomic theory freely, admires it, recognizes in it an indispensable tool, but never forgets it is a theory. But why force the majority of students to spend time and thought readjusting their early ideas when it is just as easy to lead them past the trap by basing the units of chemistry on facts without the use of theory? For this reason only, and not at all from a lack of appreciation of the atomic theory, some pains have been taken to develop our units from the laws alone, without reference to any theory, in the following pages.

Ratios. The results of analysis are expressed in percentage. They are ratios, giving the parts by weight with which each element enters into the compound. A ratio is not altered by multiplying or dividing it by any number. It was a truly brilliant idea to try multiplying and dividing these ratios until each element was represented in all ratios in which it appeared, by one characteristic number, or a small whole number multiple of the characteristic number. Results of analysis and simplified ratios for four substances are as follows:

Water: 11.11 per cent hydrogen; 88.88 per cent oxygen..... = 1 : 8
Hydrogen peroxide: 5.9 per cent hydrogen; 94.1 per cent oxygen.. = 1 : 16
Methane: 25 per cent hydrogen; 75 per cent carbon..... = 1 : 3
Carbon dioxide: 27.3 per cent carbon; 72.7 per cent oxygen..... = 3 : 8

Dividing the first three ratios through by numbers such as, in each case, to make the number representing parts by weight with which hydrogen enters into combination equal to one, we obtain the ratios after the equality marks. Oxygen appears in the first ratio with the value 8, in the second with the value 16. Eight appears to be the characteristic number for oxygen. Divide the fourth ratio through by such a number as to make the oxygen value 8 and that gives us 3 for carbon. This is the same number we obtained for carbon when we altered the third ratio in such a way as to represent the hydrogen in it by 1. If this were all the data we had, we should say the characteristic numbers were 1 for hydrogen, 8 for oxygen, and 3 for carbon.

We have an immense amount of data, every analysis gives us a ratio, and we can manipulate them all in this way. The more we bring into consideration, the more clearly evident it is that we can select a number for each element such that it, or some small number multiple of it, expresses the parts by weight with which that element enters into all its known chemical compounds.

Symbols. For the sake of brevity we do not write the full names of the elements, but only the initial, or the initial and one other letter, when confusion might otherwise arise, of its Latin name. We call these the symbols.

Formulæ. Now if, besides the name, we let each symbol stand as an algebraic symbol for that number which is so characteristic of each element, the parts by weight with which it enters into combination, we have a system which enables us to compress an immense amount of information into small space. We may then combine symbols into formulæ which will tell us not only what elements are present in the compound, but also the parts by weight of each element there. The sum of the symbol weights in the formula will then be the formula weight.

Equations. Such formulæ can be combined into equations representing reactions, and these enable us to carry out a great variety of useful calculations. But before a calculation can be begun the equation must be "balanced," *i.e.*, the smallest possible coefficients are placed before the formulæ until there are as many of each symbol to the right as to the left of the equality mark. This is necessary, for experience has taught us that no mass is lost in any chemical reaction.

Use of Arrows. Sometimes we have no intention to make a calculation and merely wish to state the substances involved in a reaction. We may place the formulæ for all the original substances in one group and for the products in another, separating the groups by a single arrow. The arrow indicates no effort has been made to "balance," for it is not an equation. Frequently reactions proceed from "right to left" under certain circumstances and from "left to right" under others. We indicate this reversibility by substituting a double arrow for the equality mark in a balanced equation.

Symbol Weights. Our task then is to select these numbers for which the symbols shall stand in such a way that all these advantages shall follow. We shall call these numbers the symbol weights. That is the best name for them, for it is utterly impossible to misunderstand it, and it does not introduce any theory.*

* It will be noticed that the term symbol weight is substituted for the present term atomic weight. Some writers use "combining weight" as synonymous with atomic weight in order to avoid the premature use of the latter term. There are two objections to this. It has been said that, as argon and helium are not known to combine with anything, we should not say they have "combining weights." This is a splitting of hairs. But other writers use the term "combining weight"

Unit for Symbol Weights. The symbol weights are based on the results of analysis and they are merely relative. Being merely relative we may choose whatever we like as the unit for measuring them. We may take any element as the standard, put its symbol weight equal to any number, and refer all others to it. We may put the symbol weight of oxygen equal to one, or of carbon equal to one, or of hydrogen equal to one; we may put the symbol weight of oxygen equal to one hundred, or to x; and then refer all others to the standard chosen.

Having perfectly free choice, let us, for the time being, set the symbol weight of hydrogen equal to one. For excellent reasons which will be stated later, and by international agreement, O = 16 has been adopted and is actually the basis for all our symbol weights. The reasoning is, of course, the same, no matter what the standard, but it is perhaps a little more readily followed if developed on the basis of H = 1. Remember that this selection is purely empirical and that we might have chosen anything else. But having made this choice, let us adhere to it.

Fractions of Symbols Excluded. We propose to combine our symbols into formulæ. It is easy to write, or to print, H_2 or H_6 when we desire to represent two or six symbol weight quantities of hydrogen in a compound. But it would be inconvenient and cumbersome if we had to represent fractional parts of symbol weights in formulæ. $H_{\frac{1}{2}}O_{\frac{1}{2}}$ is a formula for water as true to the facts as H_2O, but there is no comparison between the convenience of the two expressions. Therefore in order that our system shall be convenient, and not in the least because of any necessity in the case, we lay down a rule for ourselves. We shall select such numbers for our symbol weights that we need never use a fractional part of a symbol weight in any formula. This is important, and is the reason for certain selections to follow.

Selection of the Symbol Weight for Oxygen. We shall now

as synonymous with "equivalent weight." It is open to either construction. This diversity in its use has literally spoiled it for the purposes of science, and it will not be used again in this book. The term "symbol weight" is not open to either objection.

Too early introduction of the term "equivalent weight" is fertile in difficulties and misunderstandings for beginners. It will be introduced first in the discussion of valence. "Atomic weight" will be introduced after the atomic theory and with exactly the meaning given to "symbol weight," plus the declaration of faith in the theory.

undertake to select a symbol weight for oxygen on the basis that H = 1.

Let us tabulate some of the possibilities according to the analysis of water, remembering that ratios are not altered by multiplication or division.

H = 1. H : O = 11.11 : 88.88.

Ratio.	Symbol weight of O.	Formula.	Formula weight.
1 : 8	8	HO	9
2 : 16	16	H_2O	18
3 : 24	24	H_3O	27
4 : 32	32	H_4O	36
etc.	etc.	etc.	etc.

Intermediate and Smaller Values Excluded. The first column contains all the ratios we are willing to consider, for we have decided to base our system on H = 1 and not admit to consideration anything but whole number multiples of our unit. This excludes all intermediate possibilities and obliges us to begin our series with a ratio in which the value for H is not less than one. If we conclude to adopt the first ratio the weight for which the symbol O stands is 8. The formula is to be a combination of symbols expressing the results of analysis and so must be HO. The formula weight must be the sum of the weights represented symbolically in the formula and so is 9. Dalton did precisely this.

Excluding Smaller Values for O. This does not exclude the possibility of selecting 4 as the symbol weight of oxygen, which would involve writing the formula HO_2 and leave the formula weight 9. But there is no limit to such possible subdivision; we might call the symbol weight of oxygen 2 and write HO_4 for water, or 1 and write HO_8, and so on. We prefer to keep our formulæ as simple as possible, and so we voluntarily make our rule more rigid. We shall adopt as the symbol weight the largest number we can, but not so large that we shall ever have to use a fractional part of a symbol in any formula. From this it follows that if, for any cause, we exclude the first ratio from consideration and adopt the second, 16 is to be chosen as the symbol weight of oxygen. The formula must express the ratio 2 : 16. Since H = 1 we must write H_2. Since O = 16, we must write O, and so we construct the formula H_2O and the formula weight is 18. If, for any cause, we exclude the first two ratios, and adopt

the third, as a consequence we must adopt O = 24, and from this follows the formula H_3O and the formula weight 27. We may go on in this way indefinitely, for though we have excluded many possibilities the series we have may be extended to infinity. We must find some way to choose between these possibilities. Bringing in the ratio obtained by analysis of hydrogen peroxide or other compounds helps us not at all.

Other analyses give us similar series of possibilities for other symbol weights, for instance:

H = 1. H : Cl = 2.74 : 97.25.

Ratio.	Symbol weight of Cl.	Formula.	Formula weight.
1 : 35.45	35.45	HCl	36.45
2 : 70.9	70.9	H_2Cl	72.9
3 : 106.35	106.35	H_3Cl	109.35
4 : 141.8	141.8	H_4Cl	145.8
etc.	etc.	etc.	etc.

H = 1. H : N = 17.54 : 82.35.

Ratio.	Symbol weight of N.	Formula.	Formula weight.
1 : 4.66	4.66	HN	5.66
2 : 9.33	9.33	H_2N	11.33
3 : 14.0	14.0	H_3N	17.0
4 : 18.66	18.66	H_4N	22.66
etc.	etc.	etc.	etc.

H = 1. H : C = 25 : 75.

Ratio.	Symbol weight of C.	Formula.	Formula weight.
1 : 3	3	HC	4
2 : 6	6	H_2C	8
3 : 9	9	H_3C	12
4 : 12	12	H_4C	16
etc.	etc.	etc.	etc.

Algebraic Analogy. We are in much the same predicament as when, stating a problem algebraically, we find we have two unknowns and but one equation. Algebra teaches us, under such circumstances, that we must look at the original problem from another point of view and obtain a second, independent equation. We do much the same

in chemistry. We approach the problem from another side and secure what amounts to a second equation.

Other Properties. There are several properties which we may, and do, use to help us in our selections, but the facts comprised in Gay-Lussac's law of combining volumes are by far the most important. They lead us to adopt a rule which makes the selection from the apparently infinite number of ratios not only possible but easy. Other properties, useful for the same purpose, such as isomorphism and Dulong and Petit's law, are relatively unimportant and are in fact used only in the few cases where the method to be described cannot be applied, or merely as corroborative evidence.

Applying the Law of Combining Volumes. Just as we have series of ratios representing parts by weight entering into combination, so we have, for gases, series of ratios representing parts by volume entering into combination. Just as the first ratios lead us to the idea of selecting characteristic weights, so the second ratios lead us to the idea of selecting characteristic volumes. We might very properly call the law of definite proportions by weight the law of combining weights, and the law of combining volumes the law of definite proportions by volume. The custom, unfortunately, is to select the two names which obscure the close analogy actually there.

The fact that one volume of hydrogen unites with one volume of chlorine to form two volumes of hydrogen chloride, and that almost as simple relationships hold in every reaction where a gas is involved, is so familiar to us it is hard to appreciate what a wonderful regularity it is.

As we chose empirically a standard of reference for parts by weight in which substances combine (H = 1) so may we choose empirically a standard of reference for parts by volume in which gases combine. We see immediately that the parts by volume with which gases unite are not different and characteristic of the different substances as are the parts by weight, but that they are all the same, or some small whole number multiple of a single volume, the same for all gases, whether elementary or compound. The system of units and notation we are constructing will be more valuable if it includes and expresses this regularity.

Tentative Plan. We must experiment a little to find out how best to include it. Naturally the first idea to occur to us would be to try as this standard of reference for parts by volume, the volume

occupied by our standard of reference for weights; *i.e.*, the volume occupied by a symbol weight of hydrogen. We may choose any system of weights whatever, tons or grains, kilograms or milligrams. We do choose grams. So our standard of reference for volumes becomes the volume occupied by one gram of hydrogen under standard conditions (760 mm., 0°). Call this volume x cm³.

We know x cm³ hydrogen unites with x cm³ chlorine to form $2x$ cm³ hydrogen chloride. According to this tentative suggestion of ours the weight in grams of x cm³ chlorine should be the symbol weight of chlorine and the weight in grams of $2x$ cm³ hydrogen chloride should be the formula weight of the compound. Actual weighings prove x cm³ chlorine weigh 35.45 grams and $2x$ cm³ hydrogen chloride weigh 36.45 grams. This all corresponds excellently with the first possible ratio from analysis and, provisionally at least, we may adopt 35.45, and not a multiple of 35.45, as the symbol weight of chlorine.

Now let us apply this promising plan to the water ratio. Our experience with hydrogen chloride inclines us to think the first ratio is likely to be the best. According to this, the symbol weight of oxygen should be 8. Actual weighings tell us eight grams of oxygen occupy $\frac{1}{2}x$ cm³. Now there are two possibilities; either a symbol weight of oxygen must be considered as occupying half the volume occupied by a symbol weight of hydrogen, or the symbol weight of oxygen must be chosen as 16. If we choose the first alternative we have x cm³ hydrogen uniting with $\frac{1}{2}x$ cm³ oxygen to form x cm³ gaseous water which weighs 9 grams. (Of course the experiments are to be carried out above 100° and the volumes calculated to standard conditions.) The conditions of the first ratio are fulfilled. But if we choose to say the symbol weight of oxygen is 16, we shall have $2x$ cm³ hydrogen uniting with x cm³ oxygen to form $2x$ cm³ gaseous water which weigh 18 grams, and the formula H_2O expresses the contents of the formula volume. The conditions of the second ratio are fulfilled. Moreover, if we adopt this second alternative we observe that the volume occupied by a formula weight in grams of hydrogen chloride is the same as that occupied by a formula weight in grams of gaseous water, an interesting coincidence.

Let us try the plan of adopting as the symbol weight the weight in grams of x cm³ on the ratios for ammonia. Actual weighing tells us x cm³ of nitrogen weighs 14 grams. Accordingly we adopt the third ratio. We find that x cm³ of nitrogen unite with $3x$ cm³ hydrogen

to form $2x$ cm^3, a formula volume of ammonia, the contents of which weigh 17 grams and are expressed by the formula NH_3. But this is the same volume we had for hydrogen chloride and for gaseous water. This seems to be something more than an interesting coincidence.

The Formula Volume. It would be merely tedious to multiply these instances more. This regularity exists for every known gaseous compound. The weight in grams of this volume, $2x$ cm^3, of every known gaseous compound is the same as one of the possible formula weights in a series from analysis. We therefore adopt as a rule to be followed in establishing the units of chemistry: The volume occupied by two symbol weight quantities of hydrogen shall be called the formula volume and shall be considered as containing a formula weight of any gaseous substance. (Of course calculated to standard conditions of temperature and pressure.) The weight of this volume of any gas must then be the formula weight. Having thus secured an independent method for determining formula weights we have a method for choosing one from the infinite series of possibilities opened by each analysis.

Numerical Value of the Formula Volume. To determine the numerical value of this formula volume, we have only to determine the volume occupied by two grams of hydrogen. By actual experiment we have found that one cm^3 of hydrogen, under normal conditions of temperature and pressure, weighs 0.000 090 gram (more accurately 0.000 089 87 gram). Then $\frac{2}{0.000\ 090}$ will give the volume occupied by two grams. In round numbers this equals 22 400 cm^3. Our formula volume is then 22 400 cm^3 or 22.4 liters, and this is one of the few numerical values which it is necessary for the student of chemistry to commit to memory.

Rule for Formula Weight. It follows that, to determine the formula weight of a substance, we have but to find the weight in grams of 22.4 liters of it, as a gas and at 760 mm. and 0°. This weight is the formula weight.*

Illustration. For instance, we find that 0.0504 gram of water (gaseous) at 120° C., and under 745 mm. pressure, occupies 92 cm^3.

* Substitute for formula weight as here defined its synonym, molecular weight, and our rule summarizes all the methods for determinations of molecular weights of gases.

Applying the gas laws we calculate what volume this weight would occupy if we could have it under normal conditions:

$$x = 92 \times \frac{745}{760} \times \frac{273}{393} = 62.66 \text{ cm}^3 \text{ at } 0^\circ \text{ and } 760 \text{ mm.}^*$$

If 62.66 cm^3 weigh 0.0504 gram what will be the weight of 22 400 cm^3? $\frac{0.0504}{62.66} \times 22\,400 = 18.01$. And so 18 is, by definition, the formula weight of gaseous water. As has been said, the second ratio is the only one which agrees with this, and that is why we select it and write the formula H_2O and say O = 16.

Other Cases. Experimental determination of the weight of a given volume of the gas at measured temperature and pressure, what is called a vapor density determination, followed by the calculation of the weight in grams of 22.4 liters at 0° and 760 mm., leads to the adoption of NH_3 as the formula of ammonia and N = 14, to the adoption of CH_4 as the formula of methane and C = 12, and so on for all gases.

Formula of Hydrogen. The formula volume of hydrogen contains two grams of hydrogen. The symbol H stands for the number, 1. To express 2, using H to do it, we must write H twice. Therefore H_2 is the formula of hydrogen.

22.4 liters of oxygen at 0° and 760 mm. weigh 32 grams. O = 16. To express 32, using O to do it, we must write O twice. Therefore O_2 is the formula of oxygen.

22.4 liters of ozone at 0° and 760 mm. weigh 48 grams. To express 48 grams we must write O three times. Therefore O_3 is the formula for ozone.

The rule is followed rigorously in all cases.

Formula of Phosphorus. A vapor density determination of phosphorus leads by this same reasoning to a formula weight, 124. Then the volume occupied by a symbol weight quantity of hydrogen, when filled with phosphorus vapor, weighs 62. We should conclude P = 62. But a determination of the vapor density of the compound of phosphorus and hydrogen known as phosphine gives the formula weight 34, which corresponds to one of the ratios from analysis; P : H = 31 : 3. This causes us to write the formula PH_3 for phosphine and to conclude P = 31. We cannot hold both conclusions simultaneously, but we do not hesitate long. Our formula volume

* For details as to this method for solving "gas problems" see Appendix.

rule has proved too serviceable to alter, and so we apply it rigorously and adopt P = 31; whence follows that the formula for phosphorus vapor is P_4. Thus we abandon entirely the first tentative plan of making symbol weights the weights of equal volumes, and put our whole reliance on the plan of making formula weights the weights of equal volumes.

Summary. The whole method may be summarized in concise form. We choose our formula weights such that they conform to two distinct definitions. First, the formula weight is the sum of the symbol weights in the formula. Second, it is the weight in grams of 22.4 liters of the substance as a gas under standard conditions of temperature and pressure. Unless *both* definitions are satisfied we have not got the formula weight.

We have also obtained a new and useful definition for symbol weight. The symbol weight of an element is the least number of grams of that element which has ever been found in 22.4 liters of any pure gas under standard conditions of temperature and pressure.*

Hypothetical Case. Sometimes one does not follow the above reasoning faithfully but unconsciously skips some essential step, because of prior knowledge of the symbol weights sought. It is therefore well to try applying it to an hypothetical problem, and thus avoid the bias due to knowing the answer.

Suppose we find that hydrogen unites with an element (*a*) in parts by weight represented by the ratio H : *a* = 1 : 4. Then we have the possible ratios and corresponding formulæ, symbol weights and formula weights:

	Symbol weight of *a*.	Formula.	Formula weight.
1 : 4	4	Ha	5
2 : 8	8	H_2a	10
3 : 12	12	H_3a	15
4 : 16	16	H_4a	20
etc.	etc.	etc.	etc.

But suppose we find 22.4 liters of the compound, as a gas at 0° and 760 mm., weigh 10 grams. Then, by definition, 10 is the formula

* These statements are not strictly correct. The gas laws do not formulate accurately the behavior of gases, and so a formula weight quantity of a gas as determined by analysis is not exactly 22 400 cm^3. The symbol weights we adopt are therefore invariably the results of analysis. The deviation is, however, never large enough to cause us the slightest doubt as to which ratio to adopt.

weight. This fixes on the second ratio and its consequences, a symbol weight of 8 for a and the formula H_2a.

Second Illustration. The elements a and b unite to form a compound containing 28.59 per cent a and 71.41 per cent b. 0.35 gram of this compound as a gas at 110° C. and 740 mm. pressure occupied 161.3 cm³. No compound is known containing less b than here present. We choose to base our system on a and have set its symbol weight equal to 10. What is the symbol weight of b and what is the formula of the compound?

The first ratio we can consider is one containing a symbol weight of a:

$$28.59 : 71.41 = 10 : x \quad \text{and} \quad x = 24.9.$$

	Symbol weight of b.	Formula.	Formula weight.
$a : b = 10 : 24.9$	24.9	ab	34.9
$= 20 : 49.8$	49.8	a_2b	69.8
$= 30 : 74.7$	74.7	a_3b	104.7
etc.	etc.	etc.	etc.

Applying the gas laws we have, $x = 161.3 \times \frac{740}{760} \times \frac{273}{383} = 111.9$, or 0.35 g. of the compound as a gas at standard conditions would occupy 111.9 cm³. Then 22 400 cm³ under the same conditions would weigh $\frac{0.35}{111.9} \times 22\,400 = 70.03$.

This is exceedingly close to 69.8, and we therefore select that ratio and say, the symbol weight of b is 49.8, and the formula of the compound is a_2b.*

We have developed the method for determining the symbol weights of the elements, and the formula weights of elements and compounds, without the slightest assistance from either the atomic or molecular theories.

Change from H = 1 to O = 16. In making measurements, it is desirable to apply the measure directly to the thing measured. Hydro-

* Another problem may be desired for practice. Analysis of a compound gave 30 per cent a to 70 per cent b. 0.25 g. of the compound, as a gas at 27.3° C. and at a pressure of 684 mm., occupied 136.9 cm³. Assume $a = 5$ as the basis and find the symbol weight of b and the formula of the compound.

Answer. The symbol weight of b is 35, and the formula of the compound is a_3b.

gen does not unite with many other elements, while we know and can analyze oxygen compounds of almost all elements. Therefore oxygen is a better standard for symbol weights than hydrogen, and an international committee has finally established this unit. It would seem logical to place the symbol weight of oxygen at one or one hundred, but this would give a series of values wholly different from those which have been in use for many years, based on H = 1. When H = 1.00, O = 15.88, or nearly 16. Therefore, if we adopt O = 16 it involves only minor changes in our values. When O is made equal to 16.000 H becomes equal to 1.008.

Adopting oxygen as our unit for symbol weights, we must of course, to be consistent, use this as the standard substance in determining our formula volume. The same reasoning which led us to measure the volume occupied by two symbol weights of hydrogen, leads us to measure the volume occupied by two symbol weights of oxygen; that is, the volume occupied by 32 grams. So our formula volume is obtained by dividing 32 by the weight of one cm^3 of oxygen, measured at 0° C., and under a pressure of 760 mm. This is equal to 0.001 429 2 gram. The division gives us, of course, the same value, nearly 22 400 cm^3.

Table of Symbol Weights. As the result of much work and thought we have the table of elements, symbols and symbol weights, on the following page. An international committee revises this table yearly.

Empirical Formulæ. The case often arises that, accepting the symbol weights as adopted and listed in the table, we wish to construct the formula from an analysis of a compound. For instance, we find that a certain substance contains 54.5 per cent carbon, 9 per cent hydrogen, and 36.5 per cent oxygen. Grant that H = 1, O = 16, and C = 12, what is the formula? Divide the whole ratio through by 9 to get a quantity of hydrogen we can represent by the symbol H, and we have: C : H : O = 6 : 1 : 4. We throw away small fractions as probably due to errors in analysis. This ratio is accurately expressed by the formula $C_{\frac{1}{2}}HO_{\frac{1}{4}}$, but this is cumbersome, and we have decided not to admit fractions in our formulæ. So we multiply the ratio by 4 and get 24 : 4 : 16. This ratio is expressed by C_2H_4O, the simplest formula we can construct conforming to the analysis. We call this the empirical formula of the compound, indicating by the word empirical that the formula corresponds to the first part of the definition, and that it may or may not

INTERNATIONAL SYMBOL WEIGHTS, 1912.*

	Symbol.	Symbol weight.		Symbol.	Symbol weight.
Aluminium	Al	27.1	Neodymium	Nd	144.3
Antimony	Sb	120.2	Neon	Ne	20.2
Argon	A	39.88	Nickel	Ni	58.68
Arsenic	As	74.96	Niton §	Nt	222.4
Barium	Ba	137.37	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	11.0	Oxygen	O	16.000
Bromine	Br	79.92	Palladium	Pd	106.7
Cadmium	Cd	112.40	Phosphorus	P	31.04
Cæsium	Cs	132.81	Platinum	Pt	195.2
Calcium	Ca	40.07	Potassium	K	39.10
Carbon	C	12.00	Praseodymium	Pr	140.6
Cerium	Ce	140.25	Radium	Ra	226.4
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.45
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium†	Cb	93.5	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.7	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gadolinium	Gd	157.3	Strontium	Sr	87.63
Gallium	Ga	69.9	Sulphur	S	32.07
Germanium	Ge	72.5	Tantalum	Ta	181.5
Glucinum‡	Gl	9.1	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	3.99	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.9	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.10	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	172.0
Lutecium	Lu	174.0	Yttrium	Yt	89.0
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			
Molybdenum	Mo	96.0			

* *Journ. Am. Chem. Soc.*, 33, 1642 (1911).

† Columbium = niobium = Nb.

‡ Glucinum = beryllium = Be.

§ Niton = radium emanation.

conform to the second part. We have again an indefinite series of possibilities which we may tabulate:

C : H : O	Formula.	Formula weight.
24 : 4 : 16	C_2H_4O	44
48 : 8 : 32	$C_4H_8O_2$	88
72 : 12 : 48	$C_6H_{12}O_3$	132
etc.	etc.	etc.

But a vapor density determination gives as a result that 22.4 liters of this substance as a gas, if we could have it as such under standard conditions of temperature and pressure, would weigh 88 grams. By definition, then, the formula weight of the substance is 88, and the second of the possibilities is the one to adopt; the formula of the substance is then $C_4H_8O_2$.

We obtain the empirical formula from analysis, but we cannot say we have *the* formula unless we have a vapor density determination as well. Some substances cannot be converted to gases at temperatures within convenient reach or without decomposition. We have learned certain regularities regarding the behavior of solutions, which will be taken up in their place, which help us out of many such difficulties.

The distinction between "formula" and "empirical formula" must be emphasized. If others would conform to the usage here suggested there could never be any misunderstanding. Readers will recognize at once that what is here called the "formula," is what is commonly called the "molecular formula."

Different branches of science find it convenient to establish special units particularly well adapted to the purpose of the science. A judicious selection of units frequently brings out relations and possibilities otherwise quite obscured. In no case is this more true than in chemistry. A large part of what is before us consists in bringing out such relations between the units of chemistry, the symbol and the formula weights, and other properties.

Having thus established these units on the secure foundation of fact with no admixture of theory, we shall proceed to an appreciative discussion of the veterans of our science, the atomic and molecular theories.

CHAPTER V

THE ATOMIC AND MOLECULAR THEORIES

Historical. The origin of the atomic theory is lost in antiquity and its history can easily be made a history of the development of chemical thought. It was held by Leucippus, 500 B.C., and by Aristotle, 384 B.C. Robert Boyle, of gas-law fame, used it freely in the middle of the seventeenth century, calling it the "Phenician Philosophy." Sir Isaac Newton appears to have considered everything as consisting of small discrete particles or corpuscles, even light. In his famous "Queries" attached to his "Opticks," published in 1701, he asks, "Have not the small particles of bodies certain powers, virtues, or forces by which they act at a distance upon one another for producing a great part of the phænomena of nature?"

Continuity and Discontinuity. Before Dalton's time the atomic theory was simply a statement of belief that matter was discontinuous. It must be either continuous or discontinuous. If continuous it must be infinitely divisible, and this is inconceivable, as was said in Chapter III. If discontinuous we should, after sufficient subdivisions, reach a particle so small it could not be further subdivided, whence the name, atom, meaning the indivisible (ἡ ἄτομος). This last particle, then, inanimate as it is, must be considered as endowed with the extraordinary ability to "wriggle away from the approaching knife." This is about as inconceivable as the other alternative.

In Favor of Discontinuity. There are, in fact, two ideas here, and the mental dissatisfaction one sometimes feels is largely due to not considering them separately. The first question is, are the substances we study granular in structure or continuous? All the evidence supports the theory that they are granular in structure. For instance, a gas fills homogeneously any space. If it consists of discrete particles, we can easily form a mental picture of these becoming further apart. But if it be continuous, it is hard to understand how such expansions and contractions as we observe in the case of gases can occur. It is hard to understand how expansions or contractions

of any substance can occur with changes of temperature unless the structure is granular.

Ultimate Constituents Unknowable. The second question is, are the granules themselves granular or continuous? If we conclude they are granular we are still confronted by the same question: are these smaller granules in turn granular? There is no answer possible, and we must acknowledge at the outset that we know nothing of ultimate constituents any more than of absolute measurements. The only trouble with the concept "atom" is the name, which invariably leads the uninitiated to think we claim to know more than we do know, or possibly can know. Particle, corpuscle, granule, almost anything else, noncommittal as to what lies further back, would be preferable to a word which, every time it is used, asserts a belief in what few to-day believe. The statement that our language contains much fossil science is, unfortunately, true.

Dalton's Contributions. Dalton was the first to apply the granular structure idea quantitatively to chemistry. He said that all atoms of one substance must be of the same size, shape, and weight, otherwise we could devise some method for sifting atoms and get coarse-grained and fine-grained oxygen, for example, as we can get coarse- and fine-grained sand. If the grains were different, other properties would be different, too, but all samples of oxygen ever investigated have shown the same group of properties. Therefore the size, shape, and weight of all oxygen atoms must be the same.* He added that atoms of different substances must be different in size and weight, and that atoms must have space between them else matter would be continuous and then it would be infinitely divisible.

Atomic Weight. An atom must have weight, and this must be a definite quantity for any given substance. We have never isolated one atom and weighed it, and therefore we do not know the weight of one atom. By the process of reasoning developed at length in the last chapter, we have reached a set of relative values which we there called symbol weights. In the light of the atomic theory, these may be named atomic weights. These terms are then synonymous, but symbol weight is preferable.

* It must be stated, parenthetically at least, that this is in the nature of an argument in a circle, for, if we do not find that same group of properties we promptly say we have not oxygen, or that our oxygen is impure. For some interesting considerations in this connection, see "Die stöchiometrischen Grundgesetze und die Atomtheorie," by W. Ostwald. *Zeitschr. f. phys. Chem.*, **69**, 506–511 (1909).

Usefulness of the Theory. There can be no two opinions as to the usefulness of the atomic theory. Our minds are so constituted that we think more surely, more quickly, if we visualize what we are thinking about. While atomic weights are but symbol weights, and these but ratios, *i.e.*, abstract, and while we can think in these abstract terms, it is unquestionably easier to construct a mental picture of little balls or packages of the different elements uniting and separating in different reactions. But we should not forget, as we thus visualize, the hypothetical nature of these globules bobbing so busily about.

Kekulé's Estimate. A saner and more conservative estimate of the reliability and utility of the atomic theory was in vogue fifty years ago than fifteen years ago. Writing in 1867, A. Kekulé, (1829–1896) than whom no one ever visualized atoms more thoroughly nor to better purpose, and who originated the "benzene ring,"* expressed himself in a way we could hardly improve to-day. He said:

> I have no hesitation in saying that, from a philosophical point of view, I do not believe in the actual existence of atoms, taking the word in its literal signification of indivisible particles of matter — I rather expect that we shall some day find for what we now call atoms a mathematico-mechanical explanation, which will render an account of atomic weight, of atomicity,† and of numerous other properties of the so-called atoms. As a chemist, however, I regard the assumption of atoms, not only as advisable, but as absolutely necessary in chemistry. I will even go further, and declare my belief that *chemical atoms exist*, provided the term be understood to denote those particles of matter which undergo no further division in chemical metamorphoses. Should the progress of science lead to a theory of the constitution of chemical atoms — important as such knowledge might be for the general philosophy of matter — it would make but little alteration in chemistry itself. The chemical atoms will always remain the chemical unit; and for the specially chemical considerations we may always start from the constitution of atoms, and avail ourselves of the simplified expression thus obtained, that is to say, of the atomic hypothesis. We may, in fact, adopt the view of Dumas and of Faraday, that *whether matter be atomic or not, this much is certain, that granting it to be atomic, it would appear as it now does.*‡

The First Deduction from the Theory. The atomic theory serves admirably the first purpose of a theory, furnishing us with a plausible explanation of the known facts comprised in the laws of definite and multiple proportions. If the elements consist of atoms,

* Kekulé's own description of how the idea of the benzene ring first came to him is entertaining reading. See *Berichte d. chem. Ges.*, 23, 1306 (1890).

† Atomicity is an old word for valence.

‡ "The Study of Chemical Composition," by Ida Freund, p. 624.

one, two, three, or more atoms of one thing can combine with one, two, three, or more atoms of another to form different compounds, and fractions of atoms will not appear. Thus the proportions by weight in which substances unite must be definite, or else whole number multiples of some least values. This of course is simply a statement of the laws of definite and multiple proportions.*

Atomic Theory Delayed Progress. The laws and the theory exerted a profound influence as soon as they were published — so great, indeed, that the law of mass action and the concept of equilibrium, which were announced a few years earlier by Berthollet, being thought to contradict them, were literally driven into oblivion, not to reappear for another half century, when they were resuscitated by Guldberg and Waage. The atomic theory thus actually retarded the progress of the science in some important directions.

Early Difficulties. In the early attempts to determine the atomic weights, many difficulties were encountered and much confusion ensued. It is worth while to consider briefly the nature of some of these difficulties.

Berzelius' Analysis of Water. J. J. Berzelius (1779–1848) passed hydrogen over red hot copper oxide, caught the water formed, and weighed it. In one experiment he collected 30.519 grams of water and found the copper oxide had lost 27.129 grams. Therefore the hydrogen in the water weighed the difference, or 3.390 grams. This gave him the ratio that the weight of hydrogen is to the weight of oxygen in water as 3.390 is to 27.129, or as 1 is to 8, but told him nothing as to how many hydrogen atoms united with how many oxygen atoms. The formula for water might be H_xO_y, and neither x nor y is determined by this analysis.

The Oxides of Copper. Again, copper unites with oxygen in two different proportions, to form the black oxide and the red oxide. Berzelius obtained by analysis the following figures: In the black oxide, Cu : O = 7.918 : 2, and in the red oxide Cu : O = 7.918 : 1. Selecting O = 16 as the basis we have the following ratios and possibilities:

* The original papers and extracts from textbooks comprising the first published statements regarding the law of multiple proportions, and the atomic theory as applied to chemistry, by John Dalton, William Hyde Wollaston, and Thomas Thomson, are assembled and reprinted in convenient form in Alembic Club Reprint, No. 2, "Foundations of the Atomic Theory," a little pamphlet of 48 pages. They may be found also in Ostwald's "Klassiker der Exakten Wissenschaften," No. 3.

	Atomic weight of Cu.	Formula.
Cu : O = 7.918 : 2		
63.34 : 16	63.34	CuO
126.68 : 32	126.68	CuO_2
Cu : O = 7.918 : 1		
126.68 : 16	63.34	Cu_2O
126.68 : 16	126.68	CuO

We thus have the pairs of formulæ, CuO and Cu_2O, or CuO_2 and CuO, and cannot tell which is the better.

The Oxides of Carbon. The two oxides of carbon furnish another illustration. The weights of carbon are to the weights of oxygen in these two compounds as 3 : 8 and as 3 : 4. Let O = 16. The ratios become:

	Atomic weight of C.	Formula.
C : O = 3 : 8		
6 : 16	6	CO
12 : 32	12	CO_2
C : O = 3 : 4		
12 : 16	6	C_2O
12 : 16	12	CO

Once more we have pairs of formulæ, CO and C_2O, or CO_2 and CO and have no reason to prefer one over the other.

Substitution Rule. A most ingenious attempt to come to a definite choice was made by Berzelius with his substitution rule. He found he could substitute chlorine for hydrogen in methane in four steps, and concluded from this there must be four atoms of hydrogen, no more and no less, in that compound. The formula then is CH_4.

Efforts with Faraday's Law. Faraday discovered that when an electrical current passes through a series of solutions, the solutes are decomposed and the products of the decomposition are deposited at the electrodes in exactly those proportions by weight in which they will unite chemically. Such quantities are called equivalent weights, and the generalization is known as Faraday's law. Efforts to utilize this fact to select atomic weights were not successful, because one and the same substance frequently has more than one equivalent weight. The two chlorides of copper gave Cu : Cl = 63.5 : 35.45,

and Cu : Cl = 31.75 : 35.45. Adopt 35.45 as the value for Cl; what value shall we ascribe to Cu? We may say Cu = 31.75, and then the formulæ become Cu_2Cl and CuCl, or we may say Cu = 63.5, and then the formulæ become CuCl and $CuCl_2$. Nothing in these experimental values enables us to choose between these possibilities.

More than enough has been said to prove how impossible it is to make definite selections of atomic weights on the basis of analyses alone, and the atomic theory by itself is an imperfect tool.

Development of Molecular Theory. Although, as was demonstrated in the last chapter, Gay-Lussac's law, announced shortly before Dalton's atomic theory, contains the means to overcome these difficulties, this was not realized until about fifty years later. The early attempts to utilize this law were held to be failures.

The Hypothesis that Equal Volumes Contain Equal Numbers of Atoms. The simple relationship between the volumes of reacting gases, taken in connection with the theory that atoms are the units which unite to form chemical compounds, immediately suggested the idea that equal volumes of gases contain equal numbers of atoms.

Conflict with the Atomic Theory. But this idea was apparently in conflict with the atomic theory. To see this clearly it must be borne in mind that the molecular theory had not as yet been suggested, and that it was as customary to speak of atoms of water, or of other compounds, as it was to speak of atoms of hydrogen or of other elements. Of course it was recognized that "atoms" of water could be split into atoms of hydrogen and of oxygen and thus the significance of the word atom (indivisibility) was not maintained, even by the originators of the theory. Moreover, the word molecule was used interchangeably with the word atom, which makes it not easy for us to follow the writings of that time.

Consider the case of hydrogen and chlorine uniting to form hydrogen chloride, as it naturally enough was considered at the time Gay-Lussac first announced his law. A given volume of hydrogen, containing a certain number of atoms of hydrogen, unites with chlorine to form a volume of hydrogen chloride twice that of the original hydrogen. If now we suppose equal volumes of gases to contain equal numbers of atoms, it is evident that we have twice as many atoms of hydrogen chloride as we had atoms of hydrogen to begin with. But each atom of hydrogen chloride must necessarily contain some hydrogen, and if we adopt the atomic theory it cannot be less than one atom. Evidently there were not enough atoms of hydrogen to go

round and so it must be a mistake to assume that equal volumes of gases contain the same number of atoms.

Although this argument appeared to be flawless, fortunately for chemistry, there were those who did not accept it as final, but felt that there was value in the suggestion that equal volumes of gases contain the same number of atoms, and endeavored to modify it in such a way that it should not contradict the assumptions of the atomic theory.

Moreover, certain other facts were well known which were not explained by the atomic theory; for instance, that hydrogen and oxygen could be mixed and would remain without effect upon each other for an indefinite time unless raised to a high temperature, and yet, when a lighted match was brought in contact with them, would react with extreme violence.

Avogadro's Theory. Avogadro, in 1811, suggested that the ultimate particles of a substance, as such, are not the atoms, but rather groups of two or more atoms. According to this theory, if we continue to subdivide a portion of a substance, say hydrogen, we shall eventually reach ultimate particles of hydrogen as we know it, but these are not atoms and are capable of further subdivision. This further subdivision, if carried out, results in the loss of the properties of the original substance and furnishes atoms, particles with properties often very different in many respects from the substance as it ordinarily exists.

Definition of Molecule. Molecule is the name we give to the hypothetical smallest particle of matter that can exist by itself and retain all the properties of the original substance.

Definition of Atom. Atom is the name we give to the hypothetical smallest particle of matter which enters into chemical combination.*

He also advanced what is generally known as "Avogadro's hypothesis" or "Avogadro's theory," namely, the plausible suggestion that equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules. It is quite erroneous to call this a law, for it is not a statement of known facts.

* In his original article: "Essai d'une manière de déterminer les masses rélative des molécules éléméntaires des corps, et les proportions selon lesquelles elles entrent dans les combinaisons," *Journal de Physique par Delamétherie*, 73, 58–76 (1811). Avogadro called what we call atoms "molécules éléméntaire."

An English translation of his article is contained in Alembic Club Reprint, No. 4, and a German translation is contained in Ostwald's "Klassiker der Exakten Wissenschaften," No. 8.

Difficulties Removed. These additions to the original atomic theory cleared away the difficulties which appeared so insurmountable at first. The simplest assumption is that each hydrogen molecule contains two atoms and each chlorine molecule likewise two atoms. These molecules may be imagined as splitting up before reacting, and then reacting in such a way that one atom of hydrogen combines with one atom of chlorine to form one molecule of hydrogen chloride. Then from one molecule of hydrogen and one molecule of chlorine are formed two molecules of hydrogen chloride, or from one liter of hydrogen and one liter of chlorine two liters of hydrogen chloride. It is remarkable that such a simple assumption, the first one would naturally try, fits in with the facts so well. No process in chemistry, in which hydrogen takes part, requires us to assume a more complicated structure for its molecule.

These additions offer also a plausible explanation of the fact that hydrogen and oxygen can exist together without interaction. We can say that in molecules of these substances the atoms are held together and thus prevented from interacting. But when heat breaks up some of these molecules, the atoms interact eagerly and the heat of their reaction disintegrates the rest. So the reaction is soon complete.

Determination of Molecular Weights. This hypothetical particle called a molecule then contains all the constituent elements of the original compound, and in the fixed proportions by weight which are characteristic of the compound. It is represented by the formula, and, having adopted the rule that each symbol stands for a symbol weight in grams, the formula stands for one molecular weight in grams. The molecular weight is the same quantity which we have already named the formula weight. The determination of molecular weights is then the determination of formula weights as described in the last chapter.*

Formula weight and molecular weight are synonymous terms, with the sole distinction that the former does not involve theory while the latter does, but is, perhaps, easier to deal with mentally. No preference need be given to one term over the other, if we fully realize the place and the limitations of theories in science.

* Descriptions of the standard vapor density methods will be given in Chapter XI. It is not desirable to interrupt our discussion of the great fundamental facts and ideas to deal with details. It will suffice for the present to remind the reader of what has been said: We have only to determine experimentally the weight, volume, temperature, and pressure of a sample of the gas, and from these calculate the weight in grams of 22.4 liters and the answer is the formula, *i.e.*, molecular, weight.

Space between Molecules. The idea sometimes occurs to students that if equal volumes of all gases are supposed to contain the same number of molecules, a molecule of hydrogen must be imagined as of the same size as that of oxygen for instance. This is not a necessary corollary, for a gas must be imagined as consisting of molecules, and also of space between them. How much of the total volume occupied by a gas is to be considered as space between molecules, and how much as occupied by the molecules, will be considered with van der Waals' equation.

"Monatomic" Gases. Because we find it necessary to assume two atoms to the molecule in hydrogen and many other gases, is not sufficient reason to assume the same structure for all. Systematic application of our rules for selecting atomic or symbol, and molecular or formula, weights led us to adopt P_4 as the formula for phosphorus vapor. Rigorous application of the rules leads us to adopt the same numerical value for the symbol weight and formula weight of gaseous mercury, sodium, and other metals with boiling points low enough for us to make vapor density determinations upon them. We call these gases "monatomic." Other reasoning corroborates these conclusions and leads us to consider argon, helium, and the other rare elements in the atmosphere as "monatomic" gases. This somewhat elaborate reasoning will also be taken up later.

Molecular Weights of Liquids and Solids. The molecular and atomic theories originated from, and are based primarily upon, the behavior of gases, but we have extended them and applied them to all substances, liquid, solid and dissolved. Regularities in the behavior of solutions, strikingly similar to the behavior of gases, have enabled us to apply the same methods to determining the formula (molecular) weights of dissolved substances; but what the molecular weight of a pure liquid or solid may be is another question. If there are molecules of liquid water reachable by a process of subdivision, and there doubtless are, for all evidence is in favor of a granular structure, we know they must contain hydrogen and oxygen in parts by weight as 1 : 8, but the correct formula may be H_2O, H_4O_2, H_6O_3, or, in short, $(H_2O)_x$. By a process of reasoning we shall take up presently, we are led to believe that the formula is probably not a higher multiple than $(H_2O)_3$.

Dulong and Petit's Law. An interesting regularity in the properties of solids has given us a rule of the same nature as our rule for selecting formula weights. P. L. Dulong (1785–1838) and A. T.

Petit (1791–1820), in 1819, observed that one of the atomic weights in each series of possibilities from analysis, multiplied by the specific heat of the element in the solid state, gave a quotient between 5.8 and 6.6 in most cases. This is a statement of fact and may therefore be called a law, but we may also consider it as a rule for selecting symbol weights, and so bring out the analogy between it and our rule for selecting formula weights.

Application to Selecting Symbol Weights. The method of applying it to the selection of symbol weights is obvious. For example, suppose we find as the result of analysis of ferric chloride that Fe : Cl = 34.43 : 65.57. Assume we have selected 35.45 as the symbol weight of chlorine and wish to select a symbol weight for iron. We determine the specific heat of iron and find it is 0.105.*

We have:

Fe : Cl.	Atomic weight Fe.	Atomic weight times specific heat.
18.62 : 35.45	18.62	1.96
37.24 : 70.9	37.24	3.91
55.85 : 106.35	55.85	5.86
74.47 : 141.8	74.47	7.82

The third ratio comes much nearer to fulfilling the requirements than any other, and therefore we adopt 55.85 as the atomic weight of iron.

Atomic Heat. Since specific heat means the heat required to raise one gram one degree centigrade, this value multiplied by the atomic weight is the amount of heat required to raise one atomic weight in grams one degree. This is called the atomic heat, and we may say that the atomic heats of all solid elements are the same, approximately 6.4.

Exceptions. The approximation is rather rough and there are a good many important exceptions. The following table contains some of these:

Element	S	P	O	Si	Gl	B	H	C
Atomic heat	5.4	5.4	4.0	3.8	3.7	2.7	2.3	1.8

The rule applies best to elements with atomic weights above 30. At high temperatures these exceptions become less marked; for in-

* Specific heats are different at different temperatures. According to Lorenz the specific heats of cast iron are: at 0°, 0.1050; at 50°, 0.1107; at 75°, 0.1136. Other observers have recorded results as low as 0.0890 and as high as 0.3243, the latter value holding at 700°.

stance, the specific heat of graphite at 977° is 0.4670, which makes the atomic heat of carbon 5.6 instead of 1.8. On the other hand, if we use specific heats determined at low temperatures, more exceptions must be added to the above list.

Neumann's Extension. F. E. Neumann, in 1831, and J. P. Joule (1818–1889), in 1844, extended the application of Dulong and Petit's law. They observed that it is possible to say the heat capacity of a solid compound is the sum of the heat capacities of the atoms in the compound. By molecular heat we mean, as the term implies, the amount of heat required to raise a molecular weight in grams of the compound one degree. Then the molecular heat equals the specific heat times the molecular weight. The following is an illustration of the way in which we apply Neumann's extension of Dulong and Petit's law.

The molecular heat of calcium carbonate, $CaCO_3$, is the sum of the atomic heats. It is then $6.4 + 1.8 + 3 \times 4 = 20.2$. We find by actual experiment that the specific heat of solid calcium carbonate is 0.203.* The molecular or formula weight of the compound is the sum of the symbol weights, or $40 + 12 + 3 \times 16 = 100$. The molecular heat is obtained by multiplying the specific heat by the molecular weight, or $100 \times 0.203 = 20.3$. The close correspondence between these values depends on the specific heat chosen, but the extension is justified.

Application of the Extension. Assume that we have decided to call the atomic weight of chlorine equal to 35.45. Analysis of mercuric chloride gives us Hg : Cl = 100 : 35.45. We find the specific heat of the solid is 0.069. We have then:

	Atomic weight Hg.	Formula.	Formula weight.	Molecular heat.	
				Formula weight times specific heat.	6.4 times number of atoms.
100 : 35.45	100	$HgCl$	135.45	9.35	12.8
200 : 70.9	200	$HgCl_2$	270.9	18.69	19.2
300 : 106.35	300	$HgCl_3$	406.35	28.04	25.6

The molecular heats in the second line agree more closely than those in the other lines, therefore we choose 200 as the atomic weight of mercury.

* Other specific heats have been observed, as low as 0.1877 and as high as 0.2204.

The Method not Applicable to Molecular Weights. The method is of no service in the selection of molecular weights, for the correspondence developed in the ratio we chose is maintained, no matter by what number we multiply the whole formula. If we double it and write Hg_2Cl_4, this doubles the molecular weight, and also the molecular heat. But the number of atoms in the formula is doubled likewise and so the molecular heat calculated by the rule is doubled. The formula might be $(HgCl_2)_x$ for all the rule can tell us.

Dulong and Petit's law is worth remembering. Suppose we wish to know the specific heat of lead. Specific heat tables may not be at hand, but symbol weight tables are practically always within reach. The symbol weight of lead is 206.9. Therefore its specific heat must be approximately $\frac{6.4}{206.9} = 0.031$.

That the symbol weights indicated by this rule are the same as those indicated by the formula weight rule shows there is some underlying regularity which we do not comprehend. Adopting the atomic theory does not lead to any better understanding of what it is. We may say, a given quantity of heat will raise one atom of any solid element through the same temperature interval; but why the heat capacity of one atom should be the same for all elements quite passes our comprehension.

Much more might be said regarding the methods which have been used in determining and selecting atomic or symbol weights. As a matter of fact, we take into consideration everything we know about an element and all its compounds before we assign these values.

Summary. We have assumed, as a plausible explanation of the facts stated by the law of definite and multiple proportions, that substances consist of atoms, packages of substance which are not split into smaller packages by any known chemical process.

We have assumed, as a plausible explanation of the facts stated by the law of combining volumes, that substances consist of molecules, usually groups of atoms, and that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. This is pure theory, but so far we have found no facts not in harmony with it. On the contrary, it furnishes us with the most plausible explanation we have of many facts. We shall, therefore, now adopt these theories as statements of well-grounded beliefs, and utilize them to the full until such time as new facts require us to alter or abandon them.

CHAPTER VI

CHEMICAL ENERGY, AFFINITY, AND VALENCE

Definition of Chemical Energy. There is a force which causes substances to combine and which holds them together, more or less firmly, in compounds. We call this chemical energy, and all chemical reactions are manifestations of it. An understanding of this, and the formulation of its modes of action as a mathematical expression, something as Newton formulated the attraction of gravitation, are the main ends of the science of chemistry. No matter what particular process we happen to be studying, we are in fact all the time trying, directly or indirectly, to reach these ends. The term "chemical energy" covers then the central and ever-present problem. We have made some progress, but are still far from our goal, in spite of earnest efforts extending over hundreds of years. The isolated facts and processes we have studied and recorded are almost countless, the generalizations we have secured covering special aspects of the problem are fairly numerous, but the single simple formulation is lacking and the science is still waiting for its Newton.

We can hardly form a just estimate of the present state of our knowledge regarding chemical energy without a little of the historic perspective. For this reason there follows an exceedingly brief sketch, touching only a few of the most noteworthy efforts, discoveries, and ideas. The occasion is taken also to review certain definitions doubtless familiar from previous courses.*

* The histories of our science make much more interesting and profitable reading than one unacquainted with them supposes. The student is urged to consult some of the following books and to add to the mere outline in this text.

"A History of Chemistry," by Ernst von Meyer, translated by George McGowan, 1906, 691 pp.; "A History of Chemical Theories and Laws," by M. M. Pattison Muir, 1909, 567 pp.; "The Study of Chemical Composition," by Ida Freund, 1904, 650 pp.; "Lectures on the History of the Development of Chemistry Since the Time of Lavoisier," by A. Ladenburg, translated by Leonard Dobbin, 1900, 373 pp.; "Der Werdegang einer Wissenschaft," by W. Ostwald, 1908, 316 pp.; "Essays in Historical Chemistry," by T. E. Thorpe, 1902, 582 pp. The authority more cited than all others is, "Geschichte der Chemie," by Hermann Kopp, 4 volumes, 1843–1847.

Parallels with Human Affections. The speculations of the Greek philosophers and the alchemists are both interesting and amusing, but they furnished nothing of practical value. They drew parallels between the chemical behavior of substances and the human affections, — amity existed between some, enmity between others, — but such imagery serves no useful purpose unless to lend a touch of humor. Robert Boyle led the reaction against these senseless allegories.*

Sir Isaac Newton (1642–1727) tried to find an analogue to the force causing chemical combination in gravitation and in electrical attraction and, failing, considered it a force *sui generis*, a conclusion which holds to-day.

Affinity Tables. It was known from the earliest times that there is a great difference in the eagerness with which different substances combine, and also that there are many instances where one substance is able to drive out another from a compound and take its place. On the basis of these facts Geoffroy † (1672–1731), in 1718, drew up the first tables of which we have record, endeavoring to arrange substances in the order of their chemical affinity. His fundamental idea was that substances could be arranged in one, two, three order, and that we could say there was a stronger attraction between number one and number fifty, for instance, than between number one and number forty-nine; also that if we have a compound of number ten and number forty and bring number nine in contact with it, number nine will drive out number ten and take its place, or number forty-one will drive out, and substitute for, number forty. Unfortunately, this and all similar tables are so full of exceptions they are not of

* **Subjective and objective measures cannot be interchanged.** In those days numerical results were few and unfamiliar. Ideas and emotions on the other hand had been the subject of much study. It was but natural that analogies based on the better known should have been tried on the less well known, that the measures peculiar to the subjective world should have been applied to the objective world. To-day we have such an abundance of numerical results that our knowledge of the objective world exceeds our knowledge of the subjective, or we think it does. It is therefore natural that we should try to apply our objective numerical results to the subjective side. But they do not fit; they cannot fit. Objective measures cannot be applied to the subjective world any more than subjective measures can be applied to the objective world. A hundred years from now our efforts to apply "natural laws" to the "spiritual world" may appear as grotesque as the efforts of the alchemists to apply "spiritual laws" to the "natural world" appear to us.

† "Table des differents rapports observés en Chimie entre différentes Substances," E. F. Geoffroy (l'ainé), *Memoires de l'Acad. des Sciences, 1718 and 1720.*

much value. We do speak of the relative activities of substances and call chlorine more active chemically than iodine, because it will drive iodine out of a compound like potassium iodide. But, on the other hand, iodine will drive chlorine out of potassium chlorate and numerous similar instances have taught us the conditions are not so simple that they can be expressed in such a table.

It is hard to determine who introduced the term affinity; by some it is attributed to H. Boerhaave (1668–1738), by others to G. E. Stahl (1660–1734), by others to Albertus Magnus, the famous alchemist. It was used in the sense in which we use chemical energy, and many now make no distinction between these terms. Reasons will presently be given demonstrating that it is advantageous to consider chemical energy as divided into factors and to reserve "affinity" as a name for the intensity factor.

Velocity of Reaction. K. F. Wenzel (1740–1793), in 1777 * introduced an idea which has been of great service to us; that of measuring the velocity of a reaction. By the velocity of a reaction he meant, and we still mean, the quantity of substance which enters into reaction divided by the time which elapses while it is so entering. If we indicate by dx the small amount of the original substance, or of one of the original substances, which disappears in the corresponding short time dt, the velocity of the reaction is given by the simple expression $\frac{dx}{dt}$. By dx we may quite as well indicate the small amount of one of the products which has appeared in the corresponding small time dt and obtain the same expression for the velocity.

Wenzel caused acids to act on equal areas of metals and measured the quantities of metal dissolved per unit time, with the thought that the chemical affinity must be greatest between the two substances showing the greatest velocities of reaction. He obtained many apparently contradictory results and was forced to admit, that even though the affinity between two substances, A and C, might generally appear to be greater than the affinity between A and another substance, B, there were also conditions under which the affinity between A and B appeared to exceed the affinity between A and C. His plan then, ingenious and useful as it was and still is, is not complete.

* Carl Friedrich Wenzel's Lehre von der Verwandtschaft der Körper mit Anmerkungen, herausgegeben von David Hieronimus Grundel. Dresden, bey Heinrich Gerlach, 1800.

Influence of External Conditions. At about the same time, T. O. Bergmann* (1735–1784) made efforts to measure, not merely the total attraction existing between two substances, but also how much of the total was to be attributed to each. As we are even now unable to so divide the total manifestation of chemical energy, it is needless to say he was unsuccessful. He contributed much to the subject, however, by calling attention to the great influence of external conditions, which sometimes exactly reverse the effects. By external conditions we mean the temperature of the system, and the pressure under which it is. He also noted the marked difference in "reactivity," depending on whether the substances be brought together as gases, liquids, or solids, or in solution. Chemical energy must be inherent in the natures of substances, but also is very evidently affected to a marked degree by their condition of aggregation. Bergmann, like his contemporary, Wenzel, and predecessors, Boerhaave and Geoffroy, endeavored to summarize his results in "affinity" tables, but these cannot be said to have much present value.†

The Law of Mass Action. The next advance was made by C. L. Berthollet (1748–1822) in 1801.‡ He described his experiments and developed his views in his "Essai de Statique Chimique," published in 1803, one of the epoch-making books of our science. In this he clearly stated what we now call the law of mass action; *i.e.*, that the velocity of a chemical reaction is proportional to the quantities present in condition to react.

Chemical Equilibrium. He gave us our idea of chemical equilibrium, that it is not a condition of rest but one in which the velocity of reaction in one direction is equal to the velocity in the opposite direction. He showed that we could force a reaction to proceed to practical completion by removing one of the products, either by causing it to go off as a gas or to fall out as a precipitate, thereby upsetting the equilibrium. He explained that phosphoric acid displaced sulphuric acid from its compounds at temperatures above 338° be-

* Upsala Transactions, Vol. III, 1775. Also "A Dissertation on Elective Attractions." Translation, London, 1785.

† Most of the data of this sort have been assembled in a book called, "Researches on the Affinities of the Elements and on the Causes of the Chemical Similarity or Dissimilarity of Elements and Compounds," by Geoffroy Martin, London, 1905. This book contains some remarkable ideas about "affinity surfaces."

‡ "Recherches sur les lois de l'affinité, par le citoyen Berthollet," Mem. de l'Institut National des Sciences et Arts. Sciences Mathématiques et Physiques, Tome troisième, Paris, Prairial An IX, pp. 1, 207, 229.

cause at that temperature sulphuric acid boils off, while phosphoric acid does not.

Strength of Acids. He described one of the methods we now employ to compare the strengths of acids, stating that if two acids compete for not enough of one base, the stronger acid will get a greater quantity than the other, and the base will divide itself between the acids, in proportion to their strengths. He could not, however, think of a way to determine this distribution analytically.

His ideas outran his experimental ability and he was far ahead of his times. Methods have been devised, one after the other, at intervals of from 10 to 50 years, and his ideas have been adopted, one after the other, as the guiding principles of "modern" chemistry. Berthollet is one of the greatest names in our science.

Unfortunately he made one mistake. Believing his own ideas to be incompatible with the law of constant proportions by weight, he attacked the latter, waged a long and bitter polemic with his countryman, J. L. Proust (1755–1826), and naturally was worsted. His defeat here resulted in his own true ideas falling into disrepute. It was a full fifty years before the work of Guldberg and Waage cleared up the misunderstanding and demonstrated that in reality there was no contradiction between the law of mass action and the law of constant proportions by weight.

Equivalence. J. B. Richter (1762–1807) published two books, "Anfangsgründe der Stöchyometrie oder Messkunst chymischer Elemente," and "Ueber die neurn Gegenstände der Chemie," in the years 1791 to 1802, in which he gave the results of his experiments upon the amounts of different acids exactly neutralized by a given amount of a base, and the amounts of different bases exactly neutralized by a given amount of an acid. This marked the first appearance of the idea that the power for chemical combination possessed by a definite quantity of one substance could be exactly *satisfied* by the power for chemical combination possessed by a definite amount of another substance; in other words, that definite quantities could be considered as equivalent to each other chemically. This is, of course, the underlying idea in the laws of definite and multiple proportions which Dalton announced ten years later.

Maximum Work. In his "Grundzügen eines thermochemischen Systems," published in 1854, Julius Thomsen (1826–1909) endeavored to find the desired measure of chemical energy in the heats of reactions. These are measures, surely, but not what we want. We

want a measure such that we shall be able from it to foretell whether a reaction will proceed or not, and in which direction. Thirteen years later P. E. M. Berthelot (1827–1907) had developed Thomsen's idea into what is known as the "principle of maximum work." According to this, a chemical reaction proceeds in such a way as to evolve the maximum heat. For instance, if A and B give the compound AB with the evolution of 1000 calories, while A and C form the compound AC with the evolution of 500 calories, then, if we have A, B, and C all together, A and B will unite to the exclusion of C. In this form there are many exceptions to this principle. All reversible reactions are obviously exceptions. All reactions would have to go to completion, and we know they go only to conditions of equilibrium. No reaction could possibly take place if it were accompanied by an absorption of heat, and yet we know many endothermic reactions. Le Chatelier and van't Hoff have altered this principle to a form which holds. Their law will be discussed in detail in later chapters.

Electrical Analogy. Some notable efforts were made to establish analogies between chemical energy and other better formulated energies.

Definite quantities of substances appear to attract each other, combine, and then cease to attract other substances. The power for combination is capable of being *satisfied.* Two bodies charged with electricity of opposite signs, as we call it, attract each other, and if they come in contact neutralize each other, or, if not in electrical contact, hold each other in such a way that they do not attract other bodies. May we then consider chemical energy as essentially the same as electrical?

Dualistic System. Berzelius constructed his dualistic system upon this electrical analogy. No matter how complex a compound, he considered it as essentially of two parts, one positive and the other negative, and wrote his formulæ accordingly. For instance, calcium sulphate, which we now write $CaSO_4$, he wrote $CaO \cdot SO_3$. The oxide of the metal was the positive half and the sulphuric acid radical was the negative half. This theory led to the construction of tables in which elements were placed in the order of their supposed electrical potentials: the most positive at one end, — these were the metals and hydrogen; the most negative at the other end, — these were all acid-forming elements. There is value in this idea and we are all familiar with "electrochemical series" of the elements.

But it was quickly recognized that the position of an element in

the table by no means tells the whole story. Whereas, according to the theory, the elements furthest apart should unite with the greatest eagerness to form the most stable compounds, there are many instances of elements close together which unite readily and form distinctly stable compounds. For instance, sulphur and oxygen stand close together in such a table, and yet the compound SO_2 is stable. A still greater difficulty arose because the dualistic theory did not harmonize with the atomic and molecular theories, which assume that it is the general rule for two like atoms to unite to form one molecule. Again, soon after the dualistic theory was suggested, organic chemistry began its remarkably rapid development, and this development was largely due to its amazingly simple and adequate structural formulæ, which do not fit in well with a "polarity" theory. So the dualistic theory was shelved.

It is a question worth serious thought whether this is not a case parallel to that which resulted in discarding the law of mass action because it was thought incompatible with the law of constant proportions by weight, or that in which Avogadro's useful idea was discarded because it was thought to conflict with the atomic hypothesis. It is strange that with such examples in our history we are so prone to repeat the same mistake. There is value in this old discarded theory. All the facts of electrolysis as summarized in Faraday's law show we must have regard for what we call the positive and negative characteristics of elements and radicals. The solution of the mystery, when it comes, will contain a good deal of this "polarity theory"; indeed signs are not lacking that many minds are now working in this channel. There is, then, a partial but not complete analogy between chemical and electrical energy.

Gravitation Analogy. The result is much the same when we attempt a comparison between the attraction of gravitation and chemical energy. The analogy appears to hold to a certain extent but is not complete. The two energies are evidently not exactly alike because chemical attractions are capable of *satisfying* each other, after which there appears to be no attraction exerted on surrounding substances. Gravitation is never so satisfied. Two objects may attract each other until they come in closest contact, but the gravitational attraction which they exert on their surroundings remains as before. We should be cautious about accepting this argument as conclusive, convincing as it seems. Newton was of the opinion that some higher power than the square was required to account for the

rapid falling off of chemical attractions, but Buffon, Berthollet, and Bergmann thought the gravitation formula adequate; and Sir William Thomson, later Lord Kelvin (1824–1907), showed how the attraction of gravitation, small as it seems, might readily become great enough through minute distances to account for the firmness with which things are held together in chemical compounds. We need only to think out some spatial distribution, or form of motion, suited to account for this curious and interesting ability to be "satisfied," to reduce not only chemical but also electrical attractions to particular manifestations of gravitation. At present these further steps are missing.

Adhesion and Cohesion. There remains the attraction called adhesion when manifested between unlike substances, and cohesion when manifested between discrete particles of the same substance; the force which causes solids to retain their shape, metal wires and rods to have their tensile strengths, and liquids to wet solid surfaces and to rise in capillary tubes. This attraction falls off much faster than inversely proportional to the square of the distance; the fourth power of the distance more nearly expresses it. There are many points of similarity between adhesion and cohesion and chemical energy, but no one as yet has succeeded in deriving from this analogy the formulation we so much want.

A Difficulty. The attraction which is manifest when substances combine is very great; why then do not the "atoms" of a solid pull themselves together until there is no space between them? If they did this, matter would be continuous, but we decided to assume matter to be granular. This is as awkward a dilemma as any we have met.

Cannot Apportion Chemical Energy. Efforts to determine the proportion of the whole manifestation of energy, when two substances combine, to be ascribed to each substance, have always failed. We cannot solve the problem because each case is too complicated and contains too many unknowns. In a simple reaction such as $H_2 + I_2 = 2\,HI$, we must consider not simply the attraction between the hydrogen and the iodine, but also the attraction between the separate atoms of hydrogen and those of the iodine, for the observed result is evidently the resultant of all three, if the atomic and molecular theories are accepted. We have then one equation and three unknowns, which of course it is not possible to solve. Moreover, this reaction goes from left to right, that is, forming hydrogen

iodide at not too high temperatures, and it goes in the opposite direction, hydrogen iodide decomposing to the elements, at higher temperatures. We do not know why nor how the chemical forces are altered by changes in the temperature. All that we can say in the present instance is that at low temperatures the attraction between hydrogen and iodine predominates over the attractions of hydrogen and of iodine within themselves.

This summary has probably made evident that our questions as to what chemical energy is, what it is like, and how it should be formulated, are difficult and complicated. We must conclude that it is as different and distinct from gravitation, electrical attraction, and cohesion or adhesion, as these are different and distinct from each other. But this does not exclude the possibility that all energies may one day be found to be essentially the same.

Such progress as has been made has resulted from close study of circumscribed portions of the field. Nowhere is a dissecting of a problem into a series of smaller ones more likely to be advantageous, more really necessary than here. There follows an effort to gain such an advantage by dividing chemical energy into quantity and intensity factors.

Division into Factors. We may write the general statement, chemical energy = intensity × capacity, and the question now is, what shall, or can, we insert in place of these general terms "intensity" and "capacity"? For intensity we must insert something which determines whether a reaction proceeds or not, and in which direction it proceeds; for capacity we must insert something which sets a limit to the action when it does take place.*

Intensity Factor. Ostwald, in his "Lehrbuch der Allgemeinen Chemie," inserts the term "affinity" for the intensity factor. One might think this mere substitution of one word for another to be in-

* It may be serviceable to have a simple illustration of a division into factors in mind. If we have a reservoir of water at a height, the amount of work we can get done by the water is determined by two factors: first, the height of the reservoir above the ground (this is the intensity factor); second, the amount of water in the reservoir (this is the capacity or quantity factor). The work we can get done is given by multiplying the height by the quantity, expressed in any convenient units. In other words, the total manifestation of energy is the product of the intensity factor into the capacity factor, and we recognize this in the familiar expression, foot-pounds. Notice that it is the intensity factor alone which determines whether any action will take place. If the intensity factor is such that action will occur, then the capacity factor enters, determining the quantity, setting the limit to such action.

significant, but it is not. Until that time, indeed in a measure since then also, the two terms, chemical energy and chemical affinity, were and are confused, often used interchangeably, as if synonymous.* We might as well use the terms heat and temperature indifferently and expect to retain clarity in our ideas.

Chemical Potential. For this reason the term "chemical potential" has been coined and stands for exactly what the term affinity should stand. It has not yet been spoiled by careless thinkers and writers and therefore it is, at present, the best name for the intensity factor of chemical energy. In this place it must suffice to say we have found relative, and it must be acknowledged, not very satisfactory, measures for it, in the velocity constants of reactions, in the conditions for equilibrium, in the conductivity of acids and bases in water solution, in the electromotive series, and so on. These measures are not only relative, but apply only when the external conditions, such as temperature, pressure, and concentration, are defined and held constant. With all our study we have not found what we want, a numerical expression for the property inherent in the nature of a substance which determines whether a reaction will take place or not.

The Capacity Factor. As regards the capacity factor of chemical energy, we are better off. Ostwald, in the "Lehrbuch" already referred to, said the capacity factor was, evidently, the amounts of the substances present in a position to react, the "active mass," as it is sometimes called; but not simply the weight in grams, nor the concentration in per cent. Symbol and formula weights are the units of quantity in chemistry, and it is therefore in these terms we should express our quantity factor. Ostwald further pointed out that, as a matter of fact, our law of constant proportions by weight is nothing more nor less than a great generalization regarding the quantity or capacity factor of chemical energy.

Significance of "Valence." This idea of Ostwald's can be carried further with profit to define precisely what we mean by valence. There is sometimes a little confusion as to the true significance of this term. The general tendency may be said to be in the direction of attributing too much objective reality to it. We wonder how it happens that an atom of hydrogen has a valence of one, an

* See the definition of "affinity" in the Century Dictionary, for example. The word is ill chosen, for its true meaning is a relationship, or resemblance, and, as we know, in chemistry "affinity" is generally greatest between most dissimilar substances.

atom of oxygen a valence of two, an atom of nitrogen a valence sometimes of three, sometimes of five, and so on, and speculate a little as to whether the atoms are provided with barbed hooks or the like.

These different valences are nothing but the necessary consequences of the artificial rules we have laid down for ourselves for the purpose of selecting symbol and formula weights. The confusion which exists as to the meaning to be ascribed to the word valence is largely due to mixing unconsciously thoughts on the capacity factor with thoughts on the intensity factor, and on chemical energy as a whole. Certainly, in no case are the advantages of this factorial system of considering energies more evident than here.

Saturated Compound. The laws of definite and multiple proportions state the observed facts that a given quantity of a given substance has a definite capacity for entering into chemical combination, a definite quantity of the power for combination, but leave untouched the other factor, saying nothing at all as to the intensity with which substances combine. When the quantity of power for combination, possessed by a given amount of a substance, has manifested itself, *i.e.*, when the substance has combined chemically with a definite amount of another substance, it cannot be made to combine with more (this is the law of definite proportions), and we say the power for combination is satisfied; the result is what we call a saturated compound. Each substance which enters into a chemical reaction has a certain quantity of this power for combination, and the fact that substances unite in definite parts by weight shows that those parts by weight possess the same quantities of this power for combination.

Diverge from Usual Method in Measuring Energies. Here we diverge from our usual custom when measuring a factor of an energy, and this is the source of the misapprehensions mentioned above. Ordinarily we find a unit for measuring the energy, and then find how many of these units are associated with one gram of the substance; we just reverse this in chemistry and find *how many grams of the substance we must take to have unit quantity of the power for combination*, and so obtain what we call equivalent weights.

Unit of Combining Capacity. Here we have experimental facts capable of numerical expression. The measurements, like all others we make, are relative only, and there is nothing whatever about the facts themselves to force us to adopt one unit rather than another. We may therefore adopt that unit which promises to be most con-

venient. We may adopt one gram of hydrogen as the unit quantity of hydrogen, and the quantity of combining ability (not intensity, not "affinity") possessed by that much hydrogen we may then say is the unit quantity of power to combine; the unit in which to measure the quantity factor of chemical energy.

Weights Possessing Unit Capacity. We find by experiment that 35.46 grams of chlorine exactly satisfy the power for combination possessed by one gram of hydrogen, and we say this much chlorine is equivalent to one gram of hydrogen. The quantity of power for combination possessed by 8 grams of oxygen, by 4.6 + grams of nitrogen, by 3 grams of carbon, are severally enough to satisfy the quantity of the power for combination possessed by our unit (one gram of hydrogen) and we say these quantities are equivalent to each other. 35.46 grams of chlorine just satisfy the power for combination of 23 grams of sodium, and as, when two things equal a third they must equal each other, the quantity of power for combination possessed by 23 grams of sodium must be the same as the quantity of that power possessed by one gram of hydrogen, we therefore say these quantities of hydrogen and sodium are equivalent to each other.

Equivalent Weights. Equivalent weights are then actually selected by this test and are the weights of the different substances which we find by experiment we must take in order to get unit quantity of chemical energy. In fact they are the weights which have numerically the same quantity factor of chemical energy as one gram of hydrogen.

The concept is not confined to elements, but is constantly used for compounds also; for instance, 40 grams of sodium hydroxide, 36.5 grams of hydrochloric acid, one-half of 98, or 49 grams, of sulphuric acid, and one-third of 98, or 32.6 + grams of orthophosphoric acid are called equivalent weights of these substances, being the weights which carry unit quantity of ability to combine, unit quantity of chemical energy.

Equivalence or Valence. In many instances the equivalent weights are those we select for the symbol weights, and we say these elements show an equivalence of one. For a time the term quantivalence was substituted for equivalence, but both these words are long and we abbreviate and say their *valence* is one; they are univalent substances. By the same sort of comparisons we find symbol weight quantities of a number of elements, such as oxygen, calcium, barium, etc., all have just twice the quantity of power to combine

possessed by our unit, a symbol weight of hydrogen. We say these elements have a valence of two, or are bivalent substances. Another group of elements, such as nitrogen, phosphorus, aluminium, etc., prove to have three times the unit capacity to enter into chemical combinations and we call them trivalent.

Definition of Valence. It is hardly necessary to go further with this list, for it is evident that "valence" is *the number of units of capacity to combine possessed by chemical unit quantity of a substance.* The concept is thus not confined to elements and in fact we are constantly stating that the valence of such and such a radical is so and so.*

Valence obviously belongs in the capacity factor subdivision of chemical energy. We may write:

$$\text{Chemical energy} = \text{chemical potential} \times \text{valence.}$$

Varying Valence. This expression enables us to form a clear idea regarding the interesting fact that the valence of a substance varies. For instance, fourteen grams of nitrogen sometimes appear to have five units of capacity for chemical combination, sometimes only three. As we have said, it is the intensity factor alone which determines whether a reaction will proceed or not, and we can formulate the behavior shown by nitrogen by saying that three-fifths of its capacity for combination is at a higher chemical potential than the other two-fifths. The whole capacity is always there, but it does not all come into play unless the potential difference is sufficient.†

We probably should have adopted the quantity factor of chemical energy exclusively as our guide in selecting symbol weights, in which case they would all have been what we call equivalent weights, if it

* Depending on whether we are deriving our prefixes from Latin or Greek we call substances univalent, bivalent, trivalent, quadrivalent, quinquivalent, sexivalent, septivalent, and octivalent; or monovalent, divalent, trivalent, tetravalent, pentavalent, hexavalent, heptavalent, and octavalent. The first set is much to be preferred. Not infrequently a jumble of the two series of terms is used. It is interesting that the symbol weight quantity of no substance shows a quantity factor greater than eight.

† It may be worth while to utilize once more our mechanical simile. Suppose we have a total of five tons of water in two reservoirs, three tons at a higher level, two tons at a lower. If the outlet of a water turbine is below the upper and above the lower of these two levels, we shall be able to utilize the water in one reservoir only; if the outlet is below both levels we shall be able to utilize the water in both reservoirs. The application of the analogy to variable valence is evident. This does not pretend to be an explanation, only a way of presenting the facts.

had not been for the fact that one and the same substance may, under different circumstances, have different equivalent weights, as was illustrated in the last chapter with the two chlorides of copper. This caused us to search for an auxiliary guide and led us to adopt our formula weight rule, and to choose as the symbol weight the least number of grams of the substance ever yet found in 22.4 liters of one of its gaseous compounds (760 mm. and 0°).

This merely selects one out of the series of possibilities for the symbol weight, obtained by multiplying some smallest ratio through by whole numbers. It therefore follows of necessity, from our arithmetical handling of the facts, that if the symbol weight is not the same as the equivalent weight, it must be some small whole number multiple of it; for we excluded all intermediate values as a matter of convenience, in order not to have to write fractions in constructing our formulæ.

We now guilelessly turn in our tracks, and applying consciously the measure which we unconsciously applied when outward bound, refind the regularities which we took very good care to establish, and are amazed.

There is then nothing particularly astonishing in the fact that the valence of hydrogen being set empirically equal to one, the valence of oxygen is two, of nitrogen three, of carbon four, etc. We have carried through a classification scheme which, as we shall see, is a great convenience, but it leaves the original problem exactly where it was. We are still confronted by the great question, why do definite quantities unite to form compounds? We might as well ask why electrically charged bodies attract and repel each other, or why the earth attracts the moon. These questions are all in the same place, at the frontier of science.

Structural Formulæ. We must now leave the safe ground of experimental fact, and, assuming the atomic and molecular hypotheses to be correct, consider the enormous extension we may give to the meaning of our formulæ by including in them symbols for valences, thus obtaining our structural formulæ.

Indicating Capacities. Our symbols stand not merely for the names of elements but also for definite weights in grams. We make them stand not only for all this, but also for the combining capacities of the quantities represented, by adding lines emanating from the symbols, one line for each unit quantity of chemical energy. Thus H— represents one gram of hydrogen capable of exerting unit quan-

tity of power for combination; —O— represents sixteen grams of oxygen and tells us it can exert two unit quantities of chemical energy; $-\overset{|}{N}-$ represents fourteen grams of nitrogen in a condition to exert three units of quantity of chemical energy; $-\overset{|}{\underset{|}{N}}=$, fourteen grams of nitrogen in a condition to exert five units quantity of chemical energy, etc. Each line, no matter from what symbol it emanates, stands for one and the same quantity (not intensity) of chemical energy.

The facts we know about the quantity factor of chemical energy, lend themselves readily to graphic representation. In constructing the formula of a compound we may write the symbols in such a way that each line emanating from one coincides with (is satisfied by) another line emanating from another symbol. Thus we write H—H, a structural formula for molecular hydrogen; H—O—H, a structural formula for molecular water; $H-\overset{H}{\overset{|}{N}}-H$, a structural formula for molecular ammonia; $H-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-H$ a structural formula for methane, etc.

Warning. It must be remembered that these structural formulæ are perfectly legitimate and extraordinarily efficient assistants in grasping, retaining, and thinking about facts so long as they are regarded solely as a beautifully ingenious system of pictographs which may be drawn to represent known facts about symbol and formula weights and the quantity factor of chemical energy. Danger of false inferences lies in crediting them with too much meaning, in assuming that they represent the mechanism of the combination and that, flattened out beneath a cover glass and viewed with a sufficiently powerful microscope, a single molecule would actually look as much like its structural formula as a map looks like the city it represents. And yet many do regard them as maps of molecules, or at least as two-dimension projections of three-dimension objects. This is going too far, and it would be safer to regard them as bearing the same relation to the object that the algebraic symbols in an equation bear to the curve the equation represents. These structural formulæ do indeed lend themselves remarkably to the expression of experimental results, but so do the algebraic equations of analytical geometry.

The lines we draw are no more like what holds things together than the printed symbols are like the actual elements.

Another important group of facts must be considered in connection with this brief historical sketch of our central problem.

Differences of State. We know almost all substances may exist as a solid, a liquid, or a gas, and in all these forms show the same percentage composition. To what shall we ascribe the marked difference in properties if not to the degree of firmness with which separate particles, each with a composition symbolically represented by the formula, are held together? This is a strong argument in favor of a granular structure. We call the force acting here, cohesion, and it is generally supposed to be distinct from the force holding the elements together.

Allotropy. We know many "elementary" substances, such as carbon or phosphorus, which exist in several forms, as diamond, graphite, and charcoal, or as yellow (white) and red phosphorus. We call the phenomenon allotropy, and the forms allotropic. We have never succeeded in analyzing these forms into two different simpler substances, and so they conform to our definition of elements. To what then shall we ascribe the marked difference in properties?

Cohesion or Chemical Energy. We are inclined to ascribe these differences also to different degrees of firmness with which separate particles are held together. But cohesion does not seem to us wholly satisfactory here; probably chemical energy also plays a part, for that is about the only way we can account for the fact that allotropic forms of the same element show different heats of combustion. Perhaps the phenomenon is due to differences in arrangement of particles in the molecules. We have no means of telling how much of the difference is due to differences in cohesion and how much to differences in chemical energy. Would it not be reasonable to say we do not know when the force ceases to be cohesion and begins to be chemical energy?

Polymorphous Forms. We know multitudes of substances, both elementary and compound, which, retaining their chemical identity, appear in different crystal forms. For instance, sulphur exists as crystals in the monoclinic and also as crystals in the rhombic system; calcium carbonate exists as hexagonal crystals (calcite) and as rhombic crystals (aragonite). Such substances are called polymorphous. To what can be ascribed these differences in form but to differences in

form existing in the smallest units which go to make up crystals, and these in turn must be due either to differences in manifestations of cohesion or chemical energy, or both. Once more it is reasonable to ask whether we need differentiate very carefully between cohesion and chemical energy.

Isomers. In 1823, J. Liebig (1803–1873) found fulminate of silver, $C_2Ag_2N_2O_2$, to have the same percentage composition as cyanate of silver, CONAg. The substances have such radically different properties, the fact was hard to accept. In 1825, Faraday discovered that benzene, C_6H_6, and acetylene, C_2H_2, have the same percentage composition. Ammonium cyanate, $NCONH_4$, has the same percentage composition as urea, $CO(NH_2)_2$. The birthday of organic chemistry has been said to fall in 1828, for in this year F. Wöhler (1800–1882) discovered that if a water solution of ammonium cyanate is warmed or simply allowed to stand, the cyanate changes to urea. This is the first of the products of life which was made synthetically from inorganic materials. Until this time an insurmountable barrier was supposed to divide products of life from the artificial products of the laboratory.

Instances of which the above are typical were discovered in rapid succession. The phenomenon is called isomerism, and the substances are called isomers. All substances which have the same percentage composition are called isomers in the broad sense of the word.

Polymers. Isomers are conveniently divided into two classes. Isomers the formula weights of which are different (multiples of some smallest value) are called polymers. For instance, the formula weight of benzene is three times that of acetylene, and we write the formulæ C_6H_6 and C_2H_2, respectively.

Metamers. Isomers the formula weights of which are the same are called metamers. As a typical instance of this we have ammonium cyanate and urea. Present usage appears to disregard the broader meaning of the word isomer and to consider it as exactly synonymous with metamer.

Atoms in Fixed Positions. The existence of metamers excludes the possibility of imagining atoms as being freely movable in molecules, and necessitates the assumption that the force which causes substances to unite to form compounds also holds these substances in some fixed positions in relation to each other.

Constitutive Properties. We therefore ascribe the difference in properties of metamers to differences in the arrangements of atoms

in the molecules, *i.e.*, to the structure or constitution of the molecule. Properties so ascribed are called constitutive.

Conventions. In constructing our structural formulæ, to represent what elements are present in a compound, also the percentage composition, and also as many as possible of its chemical and physical properties, we have adopted a series of conventions. When a substance shows the chemical properties which cause us to call it an alcohol, the convention is to write the structural formula in such a way that it shall contain at least once the combination of symbols, —O—H. When it shows the chemical properties which cause us to call it an aldehyde, the convention is to write its structural formula in such a way that it shall contain at least once the combination

of symbols, —C=O, and so on. It is perfectly correct to say that

—C=O spells the word aldehyde in chemical pictographs, but it would be confusing fact with theory to state as a fact that atoms are actually in those positions.

Classification of Organic Chemistry. A great number of these conventions have gradually come into existence. Just why these particular conventions have been adopted rather than others, is a large part of the immense subject of organic chemistry, better called the chemistry of the carbon compounds, into which we have not time to enter. The reader is referred to any of the numerous excellent texts for countless illustrations of ingenious interweaving of symbols for atoms with symbols for valence to represent experimental facts.

Caution. If objective reality is attributed to the lines representing valences, as is frequently done when they are referred to as "bonds" or "ties," false inferences are hard to avoid. Following out the mechanical analogy, one would think two atoms held together by two or more "bonds" would be held together more firmly than two atoms held together by one. In general, the reverse appears to be the case, and according to experimental evidence a complicated molecule shows a greater inclination to split apart at the "double bond" than elsewhere.

These "bonds" or "ties" do not indicate the firmness with which substances cling together, or the stability of the compound. In other words they tell us nothing of the *intensity* of chemical energy, but as

has been said, represent solely the number of units of *capacity for combination.*

The moment we try to be more explicit as to what these lines stand for, we get into inextricable difficulties. One line may stand for a line of force, or twenty lines of force, or ten thousand of them; it may stand for "a direction of preference," even a protuberance on an atom or a cavity in it, or for something else the mind of man has never yet conceived. Speculation here has been rife, but uniformly futile. We shall revert to the subject of structural formulæ in connection with other properties, the refraction of light, and the rotation of the plane of polarized light by certain substances.

Summary. In this brief and incomplete quasi-historical review we have learned that the many efforts to find out what chemical energy is, what it is like, and how it should be formulated have met with but qualified success. We recognize that it is not like any other form in all particulars, but partakes of the characteristics of several other forms in some particulars. We have found that it simplifies the problem somewhat if we dissect it into factors. The quantity factor, valence, indissolubly bound up with our symbol and formula weights, has enabled us to establish a truly wonderful classification of the elements, as will be seen in the next chapter. Further consideration of the intensity factor will be deferred until we begin the systematic study of processes.

CHAPTER VII

THE PERIODIC SYSTEM

As soon as tables of the atomic weights were first published, it became a subject for speculation whether any relation could be discovered between these numbers.

Prout's Hypothesis. W. Prout (1786–1850), an English physician, in 1815 advanced the interesting hypothesis generally known by his name. Many atomic weights are very nearly whole numbers when hydrogen is put equal to one. He suggested that these small differences were probably errors and that all substances were but compounds of one "mother substance," namely, hydrogen, and an atom of carbon, for instance, was to be considered as an aggregation of twelve atoms of hydrogen. The atomic weight of calcium is 40.07;* that of fluorine 19.0; that of phosphorus 31.04; of sulphur 32.07; of nitrogen 14.01; etc. But other atomic weights fall nearly in the middle between two whole numbers. For instance the atomic weight of chlorine is 35.46, that of strontium is 87.63, etc.

J. S. Stas (1813–1891) determined some atomic weights with such care that his greatest possible experimental error was less than the difference between them and whole numbers. This disproved Prout's hypothesis as originally stated. But then J. B. Dumas (1800–1884) suggested one-half the atomic weight of hydrogen as the fundamental unit, and when Stas demonstrated his experiments excluded this possibility, Dumas suggested one-fourth the atomic weight of hydrogen. There being no limit to such suggestions reduced the discussion to an absurdity and the hypothesis was abandoned.

The Idea Survives. It is exceedingly interesting that Prout's fundamental idea will not stay down, but crops up in new forms. In 1901 Strutt† calculated by the theory of probabilities what the

* The atomic weights given in this chapter are those of the table based on O = 16. They illustrate the facts quite as well as those based on H = 1. It is desirable to become familiar with the actually adopted numbers, and insertion of two sets of values would do more harm than good.

† R. J. Strutt, *Phil. Mag.* (6), 1, 311–314 (1901).

chances were that the symbol weights would come as close as they do come to whole numbers. He found that the chance was not more than one in one thousand, and therefore the observed approximation is not accidental, but indicates some fundamental facts of nature which have not as yet been discovered. The corpuscular or electron theory contains the same idea of a "mother substance."

Doebereiner's Triads. The nucleus from which our present periodic system started is a regularity first noticed by J. W. Doebereiner (1780–1849). In 1817,* he observed that groups of three elements could be selected, all the elements in one group being similar chemically, and having atomic weights such that the atomic weight of the middle member is the arithmetical mean of the values of the extreme members. For instance, the atomic weight of lithium is 6.94, that of sodium 23.00, that of potassium 39.10. The difference between the atomic weight of lithium and that of sodium is 16. The difference between the atomic weight of sodium and potassium is again 16. Thus there is a constant difference in the atomic weights of the succeeding members of this triad. Chlorine, bromine, and iodine form another such group, and sulphur, selenium, and tellurium a third. The following tabulation shows the nearly constant difference between successive members of these triads.

Li= 6.94		Cl= 35.46		S= 32.07	
	16.06		44.56		47.13
Na=23.00		Br= 79.92		Se= 79.2	
	16.10		47.00		48.3
K=39.10		I=126.92		Te=127.5	

This constant difference in the values of the symbol weights of the succeeding members of these groups is something similar to the constant difference observed between successive members of any one of the numerous homologous series of organic chemistry. For instance, we have methane, CH_4, with a formula weight of 16, ethane, C_2H_6, with a formula weight of 30, propane, C_3H_8, with a formula weight of 44, and so on. There is a constant difference of 14 between the formula weights of the succeeding members.

Other groups of three elements have almost the same symbol weights, and the properties of all the elements in one of these groups are as similar to each other as these weights. For instance:

* *Gilbert's Annalen*, **26**, 331 (1817).

Fe=55.85	Ru=101.7	Os=190.9
Co=58.97	Rh=102.9	Ir=193.1
Ni=58.68	Pd=106.7	Pt=195.2

All these groups of three are known as Doebereiner's triads.

That there is some connection between the symbol weights and other properties of the elements was very evident and a number of chemists endeavored to formulate this connection. An effort was made by Dumas;* and suggestions made by B. de Chancourtois in 1862 and 1863 closely resemble the system of classification finally adopted.†

Law of Octaves. In 1864, J. A. R. Newlands observed that when the elements are arranged in the order of their symbol weights, the eighth is very similar, chemically, to the first; the ninth to the second; the tenth to the third; and so on. This generalization goes by the name of Newlands' Law of Octaves.‡

Newlands did not stop here but, in 1866, arranged the elements in a table, which, while not so good as later tables, deserves recognition as one of the first attempts at a periodic system. His efforts were ridiculed, and his paper was returned to him as unsuited for publication.§

The Periodic Table. In 1869, Lothar Meyer (1830–1895) in Germany, and D. I. Mendelejeff (1834–1907) in Russia, simultane-

* *Annal. de Chim. et de Phys.* (3), **55**, 209 (1859).

† See Chapter XIII of "History of Chemical Theories and Laws," by M. M. P. Muir for an interesting historical account and numerous references.

‡ "In other words, the eighth element starting from a given one is a kind of repetition of the first, like the eighth note of an octave in music." J. A. R. Newlands, *Chem. News*, **10**, 94 (1864). "Thus in the nitrogen group, between nitrogen and phosphorus there are 7 elements; between phosphorus and arsenic, 14; between arsenic and antimony, 14; and lastly, between antimony and bismuth, 14 also. This peculiar relationship I propose to provisionally term the 'Law of Octaves,'" *ibid*, **12**, 83 (1865).

§ "The grand point I have contended for, and do contend for, is the existence of a simple relation among the elements when arranged in the order of their atomic weights." . . . "On March 1, 1866, I read a paper on the subject before the Chemical Society; and at that time the mere notion of anyone even seeking to find a simple relation among the elements when arranged in their natural order was looked upon as so absurd that one of the most distinguished members of the Society [Prof. G. F. Foster, see *Chem. News*, **13**, 113 (1866)], asked me 'if I had ever examined the elements according to the order of their initial letters.' My paper was returned to me as 'not adapted for publication in the Society's Journal.'" Newlands, *Chem. News*, **32**, 22 (1875).

ously, and independently, published tables practically the same as those with which we are familiar.*

A Graphic Representation of the Law of Octaves. The table, as it stands to-day, is reproduced on the opposite page. The elements are put in the order of their symbol weights, and, leaving He, Ne, and A out of consideration for the present, when seven have been written, the eighth is placed beneath the first, and so on. This, the fundamental idea, is a graphical expression of Newlands' law of octaves, but it must be modified in several particulars.

Hydrogen has to stand alone, it has no analogue. The first fourteen elements form pairs with remarkable correspondences. Lithium and sodium, carbon and silicon, oxygen and sulphur, fluorine and chlorine are chemically very similar.

Chemical Properties. Gradation from Alkaline to Acid. If we consider the vertical columns numbered from one to seven, we find that in number one we have sodium, potassium, etc., the elements present in our strongest alkalies. Column number two contains the metallic elements of our alkaline earths, so-called. The oxides of the elements in column number three are basic, but not strongly so. The oxides of the carbon group in column number four are somewhat acid. The elements in column number five form distinctly acid oxides, and those in column number seven give us our strongest acids.

Passing then from left to right along a horizontal row, we pass from the most pronounced alkaline or basic properties through gradual changes to the most pronounced acid properties. If we go back and begin over again on the second horizontal row, we meet again the same pronounced alkaline properties which shade over to acid properties as before. That is to say, the same properties recur periodically. It is this periodicity, or recurrence, of properties which gives the table and the law their names.

Valence with Reference to Oxygen. Another property showing this regular change and periodic recurrence is the valence of the elements. The valence with reference to oxygen increases by one from column to column, until it reaches a maximum of seven, when we must go back to where we started, and have again a valence of one. For example, we have the compounds Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, Cl_2O_7, and then we go back to K_2O.

* The student is advised to read "An Attempt toward a Chemical Conception of the Ether," by Mendelejeff (1904). It is a pamphlet of 50 pages containing the latest views of him to whom we owe so much of our periodic classification.

PERIODIC TABLE

Series.	Group 0.	Group I. RH R_2O	Group II. RH_2 RO	Group III. RH_3 R_2O_3	Group IV. RH_4 RO_2	Group V. RH_3 R_2O_5	Group VI. RH_2 RO_3	Group VII. RH R_2O_7	Group VIII. RO_4
1	.....	H= 1.008	.....	.....	.....	.....	.....	.....	.....
2	He= 3.99	Li= 6.94	Gl*= 9.1	B=11.0	C=12.00	N=14.01	O=16.000	F=19.0	.....
3	Ne=20.2	Na=23.00	Mg=24.32	Al=27.1	Si=28.3	P=31.04	S=32.07	Cl=35.46	.....
4	A=39.88	K=39.10	Ca=40.07	Sc=44.1	Ti=48.1	V=51.0	Cr=52.0	Mn=54.93	Fe=55.84, Ni=58.68, Co=58.97
5	.....	Cu=63.57	Zn=65.37	Ga=69.9	Ge=72.5	As=74.96	Se=79.2	Br=79.92	.....
6	Kr=82.92	Rb=85.45	Sr=87.63	Yt=89.0	Zr=90.6	Nb*=93.5	Mo=96.0	.....	Ru=101.7, Rh=102.9, Pd=106.7
7	.....	Ag=107.88	Cd=112.40	In=114.8	Sn=119.0	Sb=120.2	Te=127.5	I=126.92	.....
8	X=130.2	Cs=132.81	Ba=137.37	La=139.0	Ce=140.25	Pr=140.6	Nd=144.3	.....	Sa=150.4, Eu=152.0, Gd=157.3
9	.....	.....	.....	Er=167.7	.....	Yb=172.0	.....	.....	.....
10	.....	.....	.....	.....	.....	Ta=181.5	W=184.0	.....	Os=190.9, Ir=193.1, Pt=195.2
11	.....	Au=197.2	Hg=200.6	Tl=204.0	Pb=207.10	Bi=208.0	.....	.....	.....
12	.....	.....	Ra=226.4	.....	Th=232.4	.....	U=238.5	.....	.....

Elements not placed in above table are Tb=159.2; Dy=162.5; Tm=168.5; Lu=174.0; Nt=222.4=Niton=Emanium=radium emanation.

* Gl=Glucinum=Be=Beryllium.

Nb=Niobium=Cb=Columbium.

Valence with Reference to Hydrogen. The elements in the first three columns do not unite readily with hydrogen, and those in the last four columns show a valence decreasing by one at each step, from four in the fourth column, to one in the seventh. For example, we have CH_4, NH_3, OH_2, FH.

Long Periods. After the first fourteen elements it is not quite such plain sailing. Alternate horizontal rows seem to be better comparable; for instance, copper and silver are more alike in their chemical properties than copper and rubidium; calcium, strontium and barium belong together; etc. So it seems expedient to arrange the elements in long periods of fourteen, and this is indicated by writing alternate elements coming in the same vertical column, first a little to the right, and then to the left, in their allotted spaces.

Postscripts of Three Elements. Even then we have groups of three elements coming as postscripts at the end of alternate periods, making each long period contain seventeen. These groups of three are "Doebereiner triads" with almost equal symbol weights, and showing marked similarity in their chemical properties. They are sometimes called transition elements, and not knowing very well what else to do with them, we establish for their convenience an eighth vertical column outside of the system proper.

The Argon Group. When the rare elements of the atmosphere were first discovered it was thought that they dealt a severe blow to the graphical system, but, as a matter of fact, they fall into the vertical column to the left of the strongest alkalies, and form what is fitly called the zero group. This heading is particularly appropriate as the elements in this group are not known to combine with anything else, *i.e.*, they may be said to have a valence of zero.

Physical Properties. We have considered enough of the facts to see clearly that, when the elements are arranged in the order of their symbol weights, the chemical properties recur at definite intervals, *i.e.*, are periodic. The majority of the physical properties are also periodic.

Curve of Atomic Volumes. The atomic volume is the volume occupied by an atomic weight in grams of a substance in the solid state. The atomic volume of an element is then its atomic weight divided by its density. For example, the density of lead is 11.3, *i.e.*, 1 cm^3 of lead weighs 11.3 grams. The symbol weight quantity, 207.1 grams, will occupy $\frac{207.1}{11.3}$ cm^3 and this (18.33) is the atomic volume of lead.

In a coördinate system we lay off atomic volumes on the ordinate, and atomic weights on the abscissa, and connecting the points thus determined, obtain the wave-shaped curve shown in Fig. 3. The recurrence of the crests and troughs of waves is a graphic representation of the periodicity of this property. Elements of similar properties are found in similar positions on successive waves of this curve.

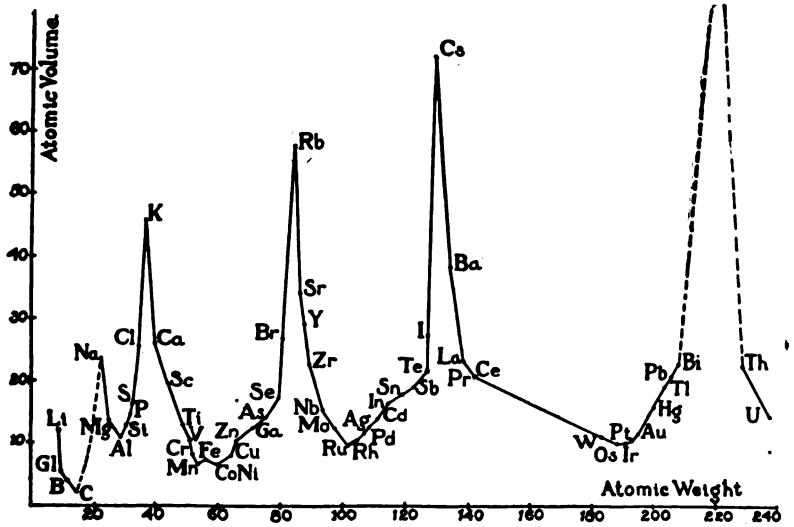


Fig. 3.

For instance, metals with strongly alkaline properties are at the summits of the waves and the halogens are on the ascending portions.

Curve of Melting Points. In another coördinate system let the ordinate represent the melting point and the abscissa represent the atomic weight. Insert the values for the elements and we obtain another curve with waves, demonstrating the periodicity of this property also. Easily fusible elements, and elements which are gaseous under ordinary conditions, are found on the rising parts, and difficultly fusible elements are at the troughs of the waves of this curve.

Curve of Density. If densities are laid off on the ordinate and atomic weights on the abscissa we have another wave-shaped curve.

Other Properties. Many other properties have been found to be of a periodic nature. The conductivity for heat and for electricity of the different elements are periodic functions of their symbol weights. Even the property of hardness appears to be periodic.

The Periodic Law. Practically every well-defined property of the elements is then proved to be a function of their symbol weights. We may combine all these facts into the one great generalization known as the periodic law: The properties of the elements, both chemical and physical, are functions of their atomic weights, and many or most of them are periodic functions.

Numerical Regularities. There are some numerical regularities too striking to be attributed to chance. Proceeding from one element to the next in the horizontal rows, the increase in the atomic weight is approximately two units in many cases. For instance, the difference Gl − Li = 2.16; B − Gl = 1.9; N − C = 2.01; O − N = 1.99.

Proceeding from one element to the next in the vertical columns the increase in the atomic weights is approximately 16, or nearly a whole number multiple of 16, in an equally remarkable number of cases. For instance, Cl − F = 16.46; Br − Cl = 44.46 ($3 \times 16 = 48$); I − Br = 47.0; S − O = 16.07; Se − S = 47.13; etc.

Of course these atomic weights are what they are simply because we took O = 16 as our basis; but whatever other substance and number might be chosen, these regularities would still exist, only the numerical values would be altered. It cannot be denied that in these regularities we have much of the underlying idea of Prout's hypothesis.

Usefulness of Law and Table. The uses of the law and table are manifold. All the elements on one side of one vertical column are strikingly similar in their properties; we say they constitute a "family." This furnishes by far the best classification we have, and it is the universal rule in texts to take up the consideration of the elements by "families."

Use in Selecting Symbol Weights. If we should discover a new element, and analyze one of its compounds, we should have a series of ratios and series of possibilities for its symbol weight. We should then select that one from these possibilities which would cause the element to fall in one of the vacant places in the table, such that its properties and those of its compounds corresponded with those of its neighbors. This is what was done in the case of indium and of glucinum (otherwise known as beryllium).

Use in Correcting Symbol Weights. If, according to the accepted symbol weight, an element falls where it clearly does not belong in the table, the chances are good that some error was made in determining the symbol weight. These considerations led to a revision of the symbol weights of molybdenum, antimony, and cæsium.

Predictions. When the table was first published, there were more vacant spaces in it than there are to-day. Mendelejeff ventured to predict the discovery of certain elements, and even went so far as to describe, rather minutely, the occurrence and properties of elements which had not been discovered. Search in the quarters thus indicated, by means of the processes thus suggested, led to the discovery of scandium, gallium and germanium. This must be considered as a truly noteworthy achievement for the periodic law and table, and at the same time one of the most beautiful illustrations of the value of generalizations in foretelling the future and for guiding research into the unknown.

Vacant Spaces. The spaces still vacant may be considered as indicating the existence of undiscovered elements, and enable us to foresee many of the properties these elements will be found to possess when they are discovered. Radioactive phenomena have taught us that some elements disintegrate and gradually disappear. Some of the vacant spaces may belong to elements which have "lived their lives" and have ceased to exist.

Exceptions to the Law. The statement we have made is the best we can make covering a truly marvelous regularity in nature, but there are some exceptions to the generalization.

Violations of the Sequence. A noteworthy exception is the position of tellurium, which, according to its symbol weight, should follow iodine, but, in the table, it precedes iodine. It is perfectly evident that chemically tellurium belongs with sulphur and selenium, and not with chlorine and bromine, while iodine belongs in the latter position. But the most careful and painstaking analyses which have yet been made continue to furnish results showing the symbol weight of tellurium as greater than that of iodine. The relative positions of argon and potassium furnish another similar exception.

Separated Pairs. Furthermore, there are pairs of elements, similar chemically, yet not in the same vertical columns; such pairs are copper and mercury, barium and lead, thallium and silver.

Other Graphical Representations. There are several other methods of representing the periodic law graphically. The simple change, making the vertical columns horizontal, and the horizontal rows vertical, is obvious. As a matter of fact this was one of the forms in which Mendelejeff first published his table. Lothar Meyer's original arrangement was substantially that which we use now.

Figure Eight. W. Crookes has suggested a descending figure eight, arranging the elements on what resembles a switch-back railroad, in such a way that the rare elements of the atmosphere fall beneath each other where the tracks cross.

Archimedes Spiral. Another arrangement has been suggested by Loew and by Erdmann. In this, ten rays are drawn through a

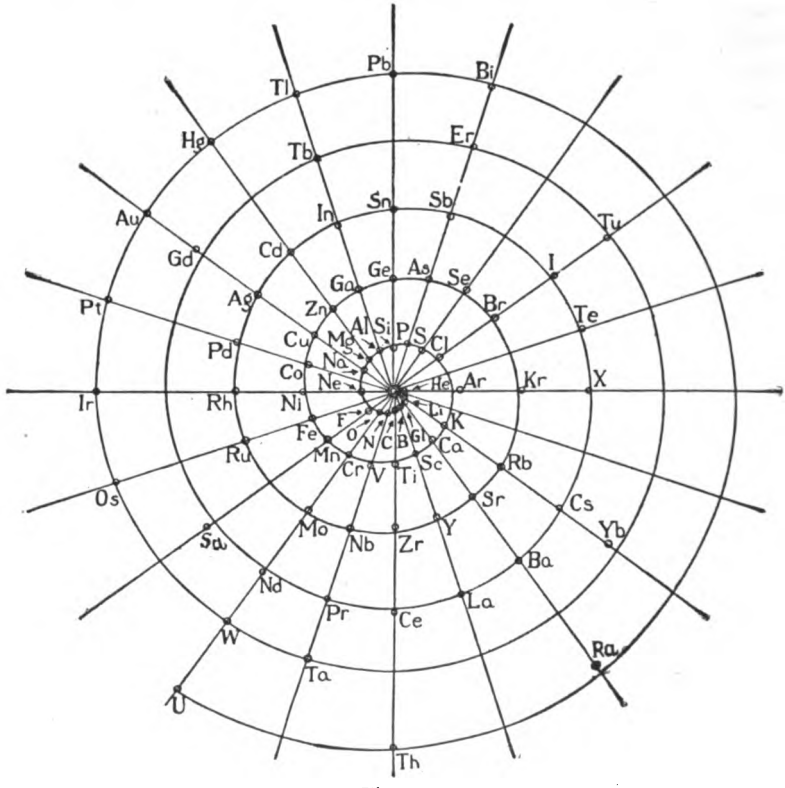


Fig. 4.

common center; thus there is an angle of 18° between each two rays. The symbol weights are laid off from the center on these rays. The points thus determined, when connected, give a nearly perfect Archimedes spiral. The two families into which each group may be divided fall on opposite sides of the same diameter. This arrangement is shown in Fig. 4.

A system has been suggested by Carey Lea on the basis of the color of the salts of the elements. The particular graphical repre-

sentation is a matter of secondary importance. But the evidence of some far-reaching basic regularity, not yet understood, is nothing short of impressive.

Discussion. The periodic law is a great, a wonderful, generalization, in that so many facts are comprised in so brief a statement. The different tables and curves are imperfect representations, and we shall doubtless be able to improve them. We can only approximate the numerical value of a given property of an element from its position in the periodic table; we cannot calculate it with mathematical accuracy. This demonstrates that there is more to learn, but we have certainly progressed far in the right direction.

As an accumulation of many facts into one law, the periodic law and system must be considered as one of the two or three most important and profitable generalizations in the science of chemistry.

Protyle. On the basis of some experimental work with yttrium, and of the striking regularities brought out by the periodic system, Sir William Crookes (1832–), in an article entitled "Genesis of the Elements," * reaffirms the plausibility of what amounts to Prout's hypothesis. He calls the simpler substance, from which all other substances may be supposed to have evolved, protyle (from πρό, earlier than, and ὕλη, the stuff of which things are made).

In his closing paragraphs he says:

> If we consider the position we occupy with reference to the primary questions of chemistry, we might compare research to a game of chess. Man, the investigator, is playing, not with Satan for his soul, but with Nature for knowledge and power. Each element has its allotted moves on the great board of the universe; some of them dependent solely on themselves, and others on the interaction of the adjacent elements. Some of our elements may be compared to pawns, others to knights, bishops, or castles. The game is fearfully unequal. Our antagonist knows the power and the limitations of every piece, all the laws of the game, all possible moves, and is merciless in exacting penalty for errors. We experimentalists know nothing but what we have learned in countless losing games. But our knowledge is increasing. Nature no longer gives us fool's mate. The struggle becomes more obstinate, more exciting, we come upon new gambits, new combinations, and though still checkmated at the last, we take a few pawns, perhaps even a piece or two. . . . But suppose we one day win the game; that we find out what these obstinate elements really are, that we learn how they came into being, and wherefore their number, their properties, and their mutual relations are such as we find them? We shall then know, *a priori*, what we have now to find out by special experiment; we shall foresee the results of every conceivable reaction, and our theories will legitimate themselves by the power of prediction. To attain such knowledge seems to me the grand task of the chemistry of the coming age.

* *Chem. News*, 55, 83–88, 95–99 (1887).

CHAPTER VIII

SPECTROSCOPIC EVIDENCES AND THE THEORY OF INORGANIC EVOLUTION

WE shall now consider some experimental facts which start trains of reasoning that do not stop at atoms, but lead yet further toward our goal, a knowledge of the ultimate constituents.

Light is an agent of great value to the chemist in the study of properties. The rate at which light is transmitted through different substances furnishes important generalizations, and sometimes what appears to be a clue to molecular, and atomic, and even "infra-atomic" structure. The three optical instruments most used in chemical laboratories are the spectroscope, refractometer, and polariscope. In this chapter we shall consider some of the facts obtained with the aid of the spectroscope, and some of the reasoning from these facts.

Refraction of Light. The velocity of light in vacuo is 180 000 miles, or 300 000 kilometers, a second.* The velocity is different in different media; the denser the medium the less the velocity. When a ray of light passes from one medium into a denser medium, it is bent out of its course; it is refracted. In Fig. 5, the horizontal line represents the surface of contact of two media, A, which might be air, and B, which might be glass. Let X represent the path of a ray in the air. After it enters B, its path is represented by Y. P, P is a perpendicular drawn through the point at which the ray strikes the bounding surface. It has been found that the velocity of light in A is to the velocity of light in B as the sine of the angle i is to the sine of the angle r. This ratio is wholly independent of the actual angle at which the ray strikes the bounding surface, and $\frac{\sin i}{\sin r}$ is a constant,

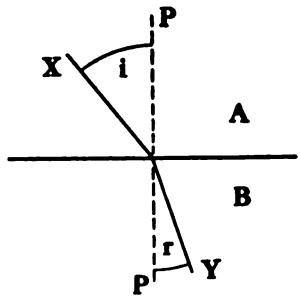


Fig. 5.

* A. A. Michelson (1852–) has determined the velocity of light to be 299 890 ± 60 kilometers a second.

called the index of refraction of the two media. It is denoted by n. Notice each medium plays a part, and it is not sufficient to say the index of refraction of a certain variety of glass is 1.423, but there should be added, "with reference to air," or "with reference to a vacuum," as the case may be. The wave length of the light should be stated also.

Dispersion. White light consists of rays of a great variety of wave lengths, and these are refracted to different extents upon passing from one medium to another. The shorter the wave length, the greater the refraction, and consequently a ray of white light is spread out, or dispersed as we call it, and we get the spectrum. A glass which has a high index of refraction does not necessarily give also a high degree of dispersion. Flint glass has a high index of refraction and the dispersion it produces is not exceptional. Crown glass has a lower power of refraction and a greater power of dispersion. Figure 6 shows the course of a ray of white light through a glass prism in which it undergoes refraction and dispersion.

Spectrum. Light with the shortest wave lengths is the most refracted, and it produces the sensation on the retina of our eyes we call violet. Light with the longest wave lengths is the least refracted, and it produces the sensation we call red. The convention is to divide the spectrum into seven color regions called in the order they follow, violet, indigo, blue, green, yellow, orange, red. A convenient way to remember this sequence is by remembering the word formed by the initials of the colors, VIBGYOR.

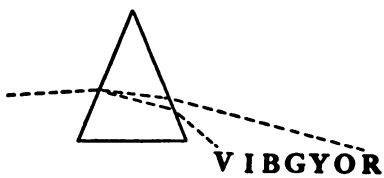


Fig. 6.

Wave Lengths. The visible spectrum is but a fraction of the whole. Visible red light may be considered as that with wave lengths lying between the values 0.76 and 0.608 μ (microns); visible violet light as that with wave lengths between 0.457 and 0.400 μ.* The wave lengths have been measured with great accuracy, but individual judgments may differ as to where the boundary lines should be drawn between the color regions, as to where violet ceases and indigo begins, where red stops and orange starts, and so on.

* Wave lengths of light are usually given in Ångström units. 0.001 mm. = 1 μ (micron) = 1000 $\mu\mu$ (millimicrons) = 10,000 Ångström units. For methods of measuring wave lengths of light, see textbooks on physics or spectroscopy.

The sun's spectrum has been shown to be continuous from wave lengths of 0.1 μ to 30 μ or about 8 octaves.

Other Wave Lengths. Heat and electricity are also radiant energy, indistinguishable from light except in terms of wave lengths. The wave lengths of dark, invisible, infra-red light lie between 0.76 μ and 300 μ; those of dark, invisible, ultra-violet light lie between 0.4 μ and 0.1 μ. Electrical waves have lengths beginning at 2 mm. (2000 μ) and reaching to a maximum limit not found as yet. There is an unmeasured region lying between 0.3 and 2 mm. (300 μ and 2000 μ). These relationships are shown in Fig. 7.

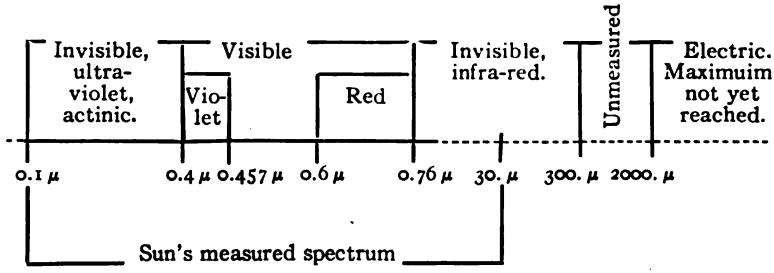


Fig. 7.

Emission of Light and Temperature. All liquids and solids, in sufficiently thick layers, upon being heated emit light, and this light contains more rays of shorter wave length the higher the temperature. They all begin to emit visible light at the same temperature. We say they are at a dull red heat, at about 525° C., and this light, examined by means of the spectroscope, shows only at the red end. As the temperature rises, the color of the object changes to bright red, to yellow, then to white, and the spectroscope shows a simultaneous extension of the visible spectrum through orange, yellow, green, blue, indigo, and violet. The white-hot liquid or solid at last gives us a continuous, unbroken spectrum.*

Some of the rare earths, notably the oxides of thorium and cerium, when heated, give us continuous spectra, but with a few particularly brilliant lines. They appear to have a selective ability to convert the energy given them into visible light, and it is for this reason that they are used in the familiar incandescent gas mantle.

* The temperature of an object may be estimated from the nature of the light it emits. First perceptible glow, 525°; dark red, 700°; beginning of cherry red, 800°; full cherry red, 900°; bright cherry red, 1000°; dark yellow, 1100°; bright yellow, 1200°; "white hot," 1300°; blue white, 1400°.

Stefan's Law. It has been found that the sum of the radiations from a perfectly black body is proportional to the fourth power of its absolute temperature. This formulation is known as Stefan's law (Josef Stefan, 1835–1893). The phrase "perfectly black body" requires a little explanation. It may be defined as a body for which the above law holds, and it does not hold for many substances. For instance, the sum of the radiations from platinum is more nearly proportional to the fifth power of its absolute temperature. But a close approximation to this theoretical perfectly black body is furnished by the interior of a box or cylinder provided with a small window through which observations can be made. This is the fundamental principle upon which the methods of optical pyrometry are based.

Bolometer. There is a region of maximum intensity of radiation in a spectrum, and it was observed by S. P. Langley, in 1886, that the position of this maximum moves further and further toward the violet end the higher the temperature.

The intensities of different portions of a spectrum may be determined by means of an instrument called a bolometer, invented by Langley. One form of this instrument consists of two short fine platinum wires about 0.01 mm. in diameter, parallel to each other and fixed in a box insulated from heat. These two wires are made two arms of a Wheatstone bridge,* and a feeble current is kept passing by means of a storage battery. An extremely sensitive galvanometer is inserted in the bridge. If one wire is a little warmer than the other, its resistance increases and a deflection is observed in the galvanometer. This instrument is remarkably sensitive and may be so constructed as to respond to a temperature difference of even less than one-millionth of a degree centigrade. One of these wires is shielded, and the spectrum to be studied is caused to "drift" slowly over the other, by moving the prism or grating which forms the spectrum. The same mechanism which moves the prism moves a sensitive photographic plate downwards. A spot of light from the galvanometer mirror is focused on this plate, and thus the deflections of the galvanometer are registered photographically. Bright lines give wide deflections; dark lines small deflections (or none) and it is a short process, after the apparatus is ready, to thus map out the intensity of a whole spectrum and to examine it at leisure.

Wien's Law. In 1894, W. C. W. Wien announced a simple relationship: The wave length corresponding to the maximum emission

* For description of Wheatstone bridge, see Chapter XXVIII.

of radiant energy by a perfectly black body is inversely proportional to its absolute temperature. Figure 8 is a diagram which might represent the result of experiments, plotting the intensity of the radiation in terms of vertical height, along a horizontal which represents the spectrum. In this diagram, the maximum intensity is shown by the vertical marked λ_m.

Fig. 8.

Wien's law may be expressed in the formula $\lambda_m \times T = A$, where λ_m is the wave length showing the maximum intensity, T is the absolute temperature, and A is a constant.

Star Temperatures. We are, then, in a position to estimate the temperature of any body which emits radiant energy. In this way, it is possible to estimate the temperatures of stars, and many appear to be far hotter than the sun. The temperature of the electric arc is estimated at between 3000° and 3500°, that of the sun as somewhat above 6000°.* Sir J. N. Lockyer† suggests the possibility that some stars may have temperatures as high as 28 000°, but this estimate is not generally accepted.

Uncertainty about High Temperatures. The accurate measurement of temperature is limited to a narrow range, from about −250° to about +1100°, the region in which we can apply thermometers which utilize the expansion of gases. Beyond these limits our uncertainty increases rapidly. For example, estimates of the melting point of platinum vary from 1720° to 1775°, and regarding higher temperatures the uncertainty is, of course, yet greater.

Line Spectra. Numerous substances cease to give continuous spectra even at relatively low temperatures. At the temperature of the bunsen gas flame, they give us, instead, few or many bright lines. Only gaseous bodies give these spectra consisting of lines, and therefore we know that the heat of the non-luminous bunsen flame is sufficient to volatilize many substances, and to cause elements which they contain to become gaseous and to emit their characteristic lights. Other elements require the higher temperature of the oxygen-hydrogen flame, or the electric arc, or the spark of an induction coil.

Spectroscopic Analysis. These line spectra are distinctly characteristic of the substances which emit them, and may be used to detect their presence. This is the basis of our methods of spectroscopic

* If nothing else is said, the centigrade temperature scale is always understood.

† "Inorganic Evolution as Studied by Spectrum Analysis" (1900), p. 174.

analysis. R. W. Bunsen (1811–1899) and G. R. Kirchhoff (1824–1887), in 1859, first introduced this method into chemistry. They found that some spectra which they observed could not be duplicated by any known elements, and this resulted in the discovery of new elements. For instance, rubidium and cæsium were discovered by Bunsen and Kirchhoff in 1861; thallium by Crookes and Laney in 1861; indium by Reich and Richter in 1863; gallium by Lecoq de Boisbaudran in 1875. And we might add argon, helium, neon, krypton, and xenon, discovered by Lord Rayleigh (1842–) and Sir W. Ramsay (1852–) between 1894 and 1898.

The spectrum of helium was observed in the corona of the sun long before the element was found on the earth.

The wide field of usefulness of the spectroscope is well illustrated by the recent experience of the Curies in their search for the source of the radioactivity they were studying. After a number of fractional crystallizations, the spectroscope revealed a faint new line. After further fractional crystallizations, this line became more brilliant, and thus acted as a guide until they obtained the new element, radium.*

Crookes' Tubes. A gas may be made to emit its characteristic spectrum under the influence of a high potential electrical current. A small amount of the gas in a rarefied condition is enclosed in a tube provided with two electrodes. When the current from an induction coil is led to these electrodes, the gas within the tube becomes luminous, though not hot, and its spectrum may be examined. Thus electrical conditions may produce the same effects as high temperatures, a fact to be remembered. If the evacuation of the tube is carried further, down to about one-millionth of an atmosphere (0.000 76 mm.) a most extraordinary change takes place. The gas ceases to emit its characteristic light and cathode rays appear. These will be considered in Chapter X. The tubes are called Crookes' tubes.

Reversal of Lines. If a vessel containing a gas is placed between the spectroscope and a source of white light, we obtain a continuous spectrum cut up by dark lines corresponding in number and position to the lines which that gas would emit. This phenomenon is spoken of as "reversal of the lines." J. Frauenhofer (1787–1826) first ob-

* Spectroscopes, both prism and diffraction grating, have been brought to a high degree of perfection. The reader is referred for details as to their construction and application in this absorbingly interesting branch of our science to "Spectroscopy," by E. C. C. Baly (1905), 568 pp. The standard work of reference is "Handbuch der Spectroscopie," by H. Kayser, in five volumes.

served such lines in the spectrum of the sun, and these have ever since been called by his name, though he did not discover their significance.

Kirchhoff's Law. This discovery was made by Kirchhoff and is stated in his law: Every glowing vapor emits light of the same wave length that it absorbs. By comparison of the Frauenhofer lines with the bright lines obtained from glowing gases we have been able, as is well known, to detect many terrestrial elements on the sun and other stars. Thus Kirchhoff is the founder of stellar chemistry.

The truly amazing results obtained in recent years have been due to the perfection of the instruments employed. By means of diffraction gratings very long spectra are produced and portions of these are photographed. The light from a distant star is faint, and when so analyzed and spread out is yet fainter. Exposures must often be made for hours, on successive nights. As many of the calculations are based upon the slight displacements of fine lines, some estimate may be made of the extreme accuracy of the clock-work mechanisms which so exactly compensate for the motions of the earth.*

Doppler Effect. The spectra of some stars show lines displaced sideways, sometimes toward the violet, sometimes toward the red. This is known as the "Doppler effect" (C. Doppler, 1803–1853). If a star is approaching us rapidly, it is nearer at each successive pulsation which goes out as light, and so the lengths of the light waves are shortened. The shorter the wave length, the more the light is refracted, and the further toward the violet end of the spectrum do we find it. If the star is receding rapidly, by the same reasoning, the wave lengths of a given light are longer than they should be, and hence a given line is displaced toward the red end of the spectrum. From these displacements, we can tell which way a star is moving with respect to us, and also the rate at which it moves.

Double Stars. This Doppler effect has been a fruitful phenomenon for astronomers. There are what are known as "double stars," two bodies, each perhaps like our sun, revolving about a common center of gravity. Some double stars are so far away that the best telescope will not show separate images. Nevertheless, the spectroscope detects the presence of two sources of light, for spectrum lines are displaced. When the two stars might be separately visible, one moving toward us, the other away from us, two lines appear where there should be but one, and these lines are on opposite sides of the

* See "The Study of Stellar Evolution," by G. E. Hale (1908).

proper position. When the two members of the double star are in line with the earth, the double line becomes one, only to separate again when the stars get out of each other's way. From such measurements, it is possible to determine the rate of rotation about the common center of gravity.

Dark Stars. A number of instances have been observed where a given line from some star moves in the spectrum in such a way as to demonstrate that the star observed is revolving about some other, although this other is absolutely invisible. In this way it has been possible to locate a large number of "dark" stars which have never been seen.

Absorption Bands. If a vessel containing a liquid or a solution be placed between the spectroscope and a source of white light, absorption bands are observed; that is, definite regions of the spectrum are dark. For instance, a solution of potassium permanganate absorbs the middle of the spectrum and lets both ends through. These absorption bands are sometimes utilized in chemical analysis.

Carbon Monoxide Poisoning. Carbon monoxide is a very poisonous gas, and poisoning by it is difficult to detect by any ordinary method of analysis. But the blood has a characteristic absorption spectrum. Carbon monoxide forms an insoluble compound with the hæmoglobin of the blood and alters this absorption spectrum materially. In this way, what would otherwise be a difficult or insoluble problem becomes exceptionally easy.

Delicacy of Spectroscopic Methods. Spectroscopic analysis is almost exclusively qualitative, and efforts to invent quantitative methods have not met with very gratifying results. It was, however, until recently, the most sensitive method known for detecting minute quantities of substances. The characteristic double yellow line has been observed when only one three-millionth of a milligram of sodium was present. It is now surpassed in delicacy by the electroscopic method for determining the presence of radioactive substances.

Spectra of Compounds. One might get the impression that there is a certain definite set of lines for each element and that the spectrum of a compound must always be a composite picture of the spectra of the elements in it. This is by no means always the case, and numerous compounds are known with characteristic spectra of their own, not additively made up of the spectra of their elements.*

* Examples: CO, CO_2, NH_3, NO_2, C_2N_2, the halogen salts of strontium, etc.

Spectra of Argon. One element may have two or even more spectra, as different from each other as are the spectra of different elements. Argon has three distinct spectra, depending upon the conditions of temperature and pressure under which the gas is.

Spectra of Iron. At what we may call low temperatures, iron gives us a continuous spectrum. At higher temperatures, we obtain what is known as the "flame" spectrum, which consists of a few lines and flutings. These flutings, which look like very carefully executed shading on a drawing, and make the spectrum look like a succession of Corinthian columns, are characteristic of all metals and other elements which require high temperature for their volatilization. And then we have also what is known as the "arc" spectrum of iron which consists, according to Rowland, of about 2000 lines. Again, we have what is known as the "spark" spectrum, in which some of these lines are much brighter. These are called "enhanced lines." At these higher temperatures some lines are dimmer, or have disappeared, and some new lines have put in an appearance. And finally, at the highest temperatures, and under conditions where lower temperatures are entirely eliminated, that is, conditions realized only on the hottest stars, we have an iron spectrum consisting of much fewer lines.*

Spectra of Hydrogen. Under a pressure of twenty atmospheres, hydrogen burning in oxygen gives a practically continuous spectrum. We obtain what is called the "first" hydrogen spectrum when we have the gas in a Crookes' tube at not too low a pressure. It consists of a series of relatively few lines.

Formulation of Series. It is a remarkable fact that the relation between the wave lengths of this series of lines may be expressed in a mathematical formula.

$$\lambda^{-1} = A\,(1 - 4\,m^{-2}) \quad \text{or} \quad \lambda = \frac{1}{A}\,\frac{m^2}{m^2 - 4}$$

where λ is the wave length and $\frac{1}{A}$ is a constant equal to 3647.20, and m is successively the small whole integers 3, 4, 5, 6, and so on to 15. The following brief table, containing only a few of many determinations, illustrates the close agreement between the results of calculation by this formula and the experimentally observed wave lengths. The values are expressed in Ångströms.

Such regularities are not confined to the spectrum of hydrogen

* See Lockyer, *loc. cit.*, p. 32.

and similar formulations have been worked out for series of lines in the spectra of other elements.

	m	Calculated.	Observed.	Difference.
$H\alpha$	3	6564.96	6564.96	0.0
$H\beta$	4	4862.93	4862.93	0.0
$H\gamma$	5	4341.90	4342.00	0.1
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
$H\mu$	14	3723.20	3722.80	−0.4 (largest difference)

The so-called "second" hydrogen spectrum consists of a great many fine lines which appear to have no connection with this formulation, and is obtained if precautions are taken not to get the hydrogen too hot.

Spectra and the Periodic Law. There is a marked similarity in the spectra of all the elements in one vertical column of the periodic system. In general, we may say the spectra of all the elements in one vertical column are nearly the same as regards the relation between the wave lengths of series of lines, but the spectrum as a whole is pushed further over toward the red end the greater the symbol weight. This relationship becomes less distinct after the first three groups, but we are amply justified in saying that the wave lengths of the light emitted by the elements in a gaseous condition are periodic functions of their symbol weights.

Stellar Evidence. With the assistance of such a formula as given for the hydrogen "first" spectrum, it is possible to calculate the positions of lines which do not appear in laboratory investigations. It is deeply interesting and significant that Lockyer * has succeeded in discovering such lines in the hottest stars. For instance, we know a number of lines characteristic of the spectrum of iron as obtained in the laboratory. We can calculate the wave lengths of other lines which we cannot produce, but, directing our spectroscope at a hot star, we find these lines. Simultaneously, other lines which were characteristic in the terrestrial system have disappeared.

Dissociated Elements. In 1873 Lockyer suggested the hypothesis that our elements do not exist in the form we know them in the hottest stars, but that at these extreme temperatures they are

* *Loc. cit.*

dissociated into simpler substances. The hypothesis of extreme heat is not essential; a high degree of rarefaction and electrical conditions similar to those in a Crookes' tube added to high temperature would produce the effect. He further suggested that as these simpler substances cool, the elements as we know them form, and thus we have a theory of inorganic evolution.

Proto Elements. These substances, whatever they are, which behave as if they were the prototypes of our familiar elements, Lockyer calls "proto" elements, and he has made observations which indicate the existence of proto hydrogen (asterium or nebulum), proto magnesium, proto calcium, proto iron, titanium, copper, manganese, nickel, chromium, vanadium, and strontium.*

There appear to be many facts connected with spectroscopic observations, the plausible explanation of which is the theory that our elements, under other than terrestrial conditions, are dissociated into simpler substances; *i.e.*, that the atoms are split into simpler objects.

Dissociation of Iron. For example, it seems impossible to avoid the hypothesis that our element iron is dissociated into simpler substances at the temperature of the sun. Masses of gas shoot out from the sun at a rate sufficient to displace spectrum lines sideways, and when the gas is the vapor of iron, we find that all the iron lines are not equally displaced. A plausible explanation for this is the assumption that the element iron in the sun consists of at least two simpler substances.

The mathematical relationship between the wave lengths of different lines shown by the formulations we have for the series of lines in the spectra of elements, particularly hydrogen, finds a plausible explanation in the hypothesis that the atoms are decidedly complicated compounds. No other plausible explanation has been advanced.

Zeeman Effect. When a luminous gas, emitting a characteristic line spectrum, is placed in a powerful magnetic field and is looked at through a spectroscope in a direction at right angles to the magnetic force, three lines are seen in place of one; the central line is in its original position and the side lines are equally distant, to the right and to the left, and these three different lights are found to be plane polarized. This is known as the Zeeman effect, from its discoverer.

* The methods, facts, and reasonings relative to this spectroscopic evidence and theory are interestingly given in "Inorganic Evolution," by Sir Norman Lockyer (1900), to which reference has already been made.

He first observed a broadening of the lines and upon increasing the magnetic field obtained these triplets.*

Charged Corpuscles Hypothesis. This effect was foreseen and described before its discovery, by H. A. Lorentz, on the basis of an hypothesis, which, by this discovery, acquires a high degree of plausibility.† This hypothesis is as follows: Suppose the source of light is rapidly-moving, electrically-charged corpuscles (Lorentz called them ions); these corpuscles are probably rotating, and in various planes. The rate of rotation must determine the wave length of the light. The rate of rotation of a charged body in a magnetic field in one plane with regard to the lines of force will not be altered; in another plane, rotation in the sense in which the hands of a watch move will be accelerated, while that in the opposite direction will be retarded. As a result, where we had originally one period of vibration, we have three.

Elements Complicated Compounds. It can be demonstrated that only if the corpuscles are as small as our other methods of estimating lead us to suppose them, will the available magnetic forces produce enough displacement to see. Since the displacement has been seen, it is plausible to assume that each line in the spectrum of an element is produced by a group of at least three electrically-charged corpuscles (probably more) vibrating with the same frequency. One element gives many lines, and so our " atom " must be an exceedingly complex system. The study of the Zeeman effect is the most promising method we have at present for learning something about the " structure of the atom."

* P. Zeeman (1865–), "On the Influence of Magnetism on the Nature of the Light Emitted by a Substance," *Phil. Mag.*, **43**, 226–239 (1897), and "Doublets and Triplets in the Spectrum Produced by External Magnetic Forces," *Phil. Mag.*, **44**, 55–60 (1897).

Looking in the direction of the magnetic force, two lines are seen and these lights are circularly polarized in opposite directions. For consideration of this case and details regarding the phenomenon consult, for example, J. J. Thomson, *Proceedings of the Cambridge Philosophical Society*, **13**, p. 39.

† H. A. Lorentz, "La Thèorie Electromagnetique de Maxwell," Leyde (1892). "Versuch einer Theorie der Electrischen und Optischen Erscheinungen in Bewegten Körpern," Leiden (1895).

CHAPTER IX

LUMINIFEROUS ETHER AND VORTEX RINGS

Luminiferous Ether. The undulatory theory of light is considered to make necessary the hypothesis of something to vibrate, a carrier of energy, a luminiferous ether. Newton suggested the existence of something of the sort.

Electromagnetic Theory. J. Clerk-Maxwell (1831–1879) found it possible to account for the properties of an electromagnetic field on the assumption that all space is filled by a luminiferous ether with just the set of properties which it is necessary to assume to account for the known phenomena of light.

Difficulties. The fact that we are led to the same conclusion by two independent lines of reasoning makes it a plausible hypothesis, but the inherent difficulties must not be overlooked. For instance, light appears to come directly from the stars, suffering no deflection as it passes through the layers of luminiferous ether just outside our atmosphere, such as it would suffer if the ether were dragged along with the earth. Therefore, it would seem necessary to assume that the earth passes through the ether without disturbing it. On the other hand, the velocity of light on the earth's surface appears to be the same whether it be measured in a direction parallel to the motion of the earth, perpendicular to it, or opposed to it. Therefore it would seem necessary to assume that the ether travels along with the earth. This is a typical dilemma.

Nature of Luminiferous Ether. Most of the attributes which we appear to be forced to assume for luminiferous ether are mutually exclusive or inconceivable. We must assume that it is homogeneous and fills all space continuously. Then it must be infinitely divisible, an inconceivability. We must assume that it is a perfect fluid offering no resistance to the passage of other bodies or parts of itself, that is, it must be frictionless. Then any motion set up in it must persist to infinity unless acted upon by another force. We must assume that it is a perfectly elastic solid, springing back to exactly its original form if deformed in any part, for it transmits light vibrations

with great rapidity and undiminished in intensity. Since it permeates all space and all substances, we are immersed in it, and it pervades us. We are like fishes in a boundless ocean, with no sense perception for water. We must assume that it is a gas, lighter than any known gas. Graetz calculated the density of the ether to be 9×10^{-16} that of water. Sir William Thomson (Lord Kelvin) calculated it to be greater than 10^{-18} that of water. Suppose it to be between these values, or 10^{-17} that of water. The weight of the air on one cm^2 at the surface of the earth is 1.033 kilograms. The weight of the ether on the same area is 0.000 000 22 mg. It must be imagined then as simultaneously, gas, liquid, and solid.

The Vortex Ring Hypothesis. Lord Kelvin suggested that we may assume the whole universe is a compound of energy and luminiferous ether as a carrier of that energy.

Now a fish, submerged in a limitless ocean, and with no sense to appreciate water, may, nevertheless, be imagined as able to detect a whirlpool in his ocean. So we may be supposed to be able to detect whirlpools in the ether. In fact, such whirlpools may be the only things that do affect our senses.

Imagine a cylinder of this "ether" extending to infinity in each direction and started revolving about its axis. As there is no friction it will revolve forever. Imagine a section of this cut perpendicular to the axis and bent in a circle till the two ends come together, the motion of revolution continuing. Here we have the simplest vortex ring imaginable, resembling a smoke ring. Nothing will stop it. It may be demonstrated mathematically that it will move out of the way of an approaching knife and will keep at a distance from similar rings. We have then here, in this vortex ring, a model atom.

We may tie knots of different sorts in our revolving ether cylinder before sticking the ends together, and, if the motions of revolution about the axis are not stopped during these manipulations, these configurations are systems which must endure to all eternity. In this way we may imagine atoms of all our elements.

These revolving figures, made of "ether" and kinetic energy, may come within each other's influence and then it can be demonstrated they will attract each other and remain together, furnishing us with our molecules, which require more or less vigorous agencies to disrupt them.

The mathematical treatment is decidedly complex, but these difficulties have been in a measure overcome, and a number of such

systems have been demonstrated to be possible. J. J. Thomson has done much towards developing the mathematical side of the subject. The greatest difficulty lies at the beginning, to imagine a substance, luminiferous ether, which carries in its train so many inconceivabilities. We hear less and less of this vortex atom theory, and more and more of the corpuscular or electron theory, the subject of the next chapter.

An Unproductive Theory. This theory, while interesting, has not been productive of new knowledge. It does not seem to have suggested many lines of work leading to new, previously unsuspected, facts. This is the test we should apply to determine the value of our theories, and by it the vortex ring theory falls to low rank.

Energy View. The day is slowly but surely coming when it will be universally conceded that all we know is energy, and that the universe consists of energy and what the philosophers term the "residuum of the unknown." This perfectly safe and conservative view would gain ground faster, but the statement that all we know is energy is often gratuitously extended till it is understood as denying the existence of anything but known forms of energy. It should not be so understood. It neither denies nor affirms that anything has an existence within the precincts of the wholly unknown. It is the opponents of the "energy" view who are constantly perpetrating the folly of making definite assertions regarding the unknown. Another obstacle to the acceptance of the energy view is the fact that we all labor in greater or less degree under a peculiar, inherent disinclination, amounting in individual cases to an inability, to conceive of energy without a carrier for it, even though our efforts to conceive of this carrier invariably lead us to vexatious dilemmas and inconceivabilities. It is only in so far as we are able to express our observations and our thoughts in terms of energy that we can avoid being led into making absurd and impossible assumptions. This is a significant fact.

CHAPTER X

RADIOACTIVITY AND THE ELECTRON THEORY

OF particular interest at the present time, owing to the quantity of new facts discovered within recent years, is the electron or corpuscular theory.*

Historical. We learned in Chapter VIII that rarefied gases enclosed in tubes, variously called Crookes, Plücker, or Geissler tubes, under the influence of high potential currents, emit light and give different spectra, and that if the evacuation is carried further, to about one-millionth of an atmosphere, a complete change occurs and the cathode sends out cathode rays perpendicular to itself, independent of the position of the anode.

These cathode rays were investigated by J. Plücker and J. W. Hittorf,† W. Crookes,‡ and others. In 1895, W. C. Röntgen (1845–) made his famous discovery of rays which pass through many substances and affect a photographic plate.§ These have been called X-rays or Röntgen rays.

Apparatus. Figure 9 shows one form of apparatus used to obtain these rays. Metallic electrodes are sealed into a glass tube, and by convention one is called the cathode (*C* in the figure), and the other the anode (*A* in the figure). The cathode is the terminal attached to

* A number of books have been published in all languages upon this subject. Comprehensive and authoritative are four books by J. J. Thomson: "The Discharge of Electricity Through Gases," (based on lectures given at Princeton University in October, 1896); "Conduction of Electricity Through Gases," (a larger book); "Electricity and Matter," (lectures delivered at Yale University in 1903); "The Corpuscular Theory of Matter," (lectures delivered at the Royal Institution in 1906); "Radioactivity," by E. Rutherford, second edition (1905), and "Traité de Radioactivité," by Madame P. Curie, 2 Vols. (1910). All journals of chemistry and physics have teemed with articles upon this topic since about 1897.

† *Phil. Trans.*, **155**, 1–29 (1865).

‡ *Phil. Trans.*, **170**, 87–164, 641–662 (1879).

§ Curiously enough the first article on this subject in a scientific journal by the discoverer himself did not appear till three years later: *Wied. Annal.*, **64**, 1–37 (1898).

the wire on which metals would deposit if, instead of producing X-rays, we used the apparatus to electrolyze a salt solution.

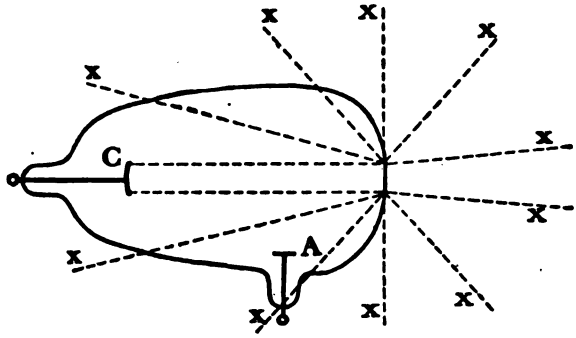


Fig. 9.

Cathode Rays. These electrodes are connected with a powerful induction coil, furnishing a rapidly alternating high potential current. The impulse in one direction cannot bridge the gap; the other can, and so the effect is as if we had an intermittent current in one direction. The gas within the tube is pumped out and, when the evacuation is sufficient, a bundle of rays are seen to shoot out perpendicularly from the cathode and strike the interior of the glass opposite, causing the glass to fluoresce at that spot. The anode is placed at one side, out of the way. These rays, inside the tube, are called cathode rays.

If a small piece of mica is placed in the path of the cathode rays within the tube, it intercepts those which strike it, and the glass so shielded does not fluoresce; the mica casts a shadow.

X-rays. At the glass the rays change in nature and do not continue in a straight line. Other rays are sent out from this fluorescent spot in every direction, as are light rays from the flame of a lamp. These rays resulting from the impact of cathode rays on the glass, or any other solid which may be in their path, can penetrate into all substances, and can pass through many, such as paper, thin sheets of aluminium, cloth, flesh, etc., and affect a photographic plate on the other side. These are the X-rays or Röntgen rays.

Absorption of X-rays. Any substance absorbs and stops X-rays to some extent, and the interesting fact has been demonstrated that the absorption is entirely independent of the chemical nature of the absorbing material, and is simply directly proportional to its density. They are wholly absorbed by thick sheets of metals, and in large

measure stopped by bones; and so we can make the now familiar, but still surprising "radiographs," photographs of the skeletons of living animals, and locate foreign substances within the body.

Fluorescent Screens. It is not necessary to use a photographic plate unless a permanent record is wanted, for X-rays, themselves invisible, striking upon sulphide of zinc or barium platinocyanide, cause these substances to fluoresce. A screen, coated with one of these substances, usually barium platinocyanide, is placed on one side of the body, the interior of which is to be investigated, and the source of X-rays on the other side. Where the rays are in a measure absorbed, the screen shines with less brilliance, and thus very striking shadow pictures are obtained.

This method is of great use in surgery, not only to locate foreign substances, but also to determine the nature of fractures of bones, and consequently its technique has been highly developed. Figure 10

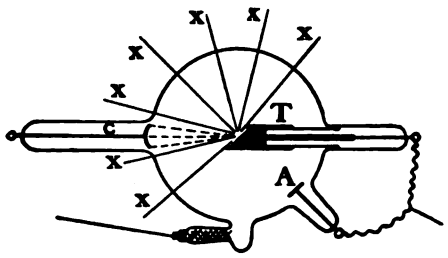


Fig. 10.

illustrates an improved tube as now used. The cathode *C* is curved in such a way that the rays come to a focus at a spot on the heavy metal "target" or "anti-cathode" *T*, which may or may not be connected with the anode. The cathode rays produced by powerful machines would soon melt glass. The focus is the center from which a hemisphere of X-rays shoots out.

Canal Rays. At the same time another set of rays arises at the anode within the tube and travels toward the cathode. If the cathode has a hole in it, these anode rays pass through and may be observed behind it. These are called the canal rays. We have then here, all told, at least three different kinds of radiant energy.

Nature of the Cathode Rays. The cathode rays must consist either of a wave motion of the luminiferous ether, or of minute particles projected from the cathode. The latter view is the more plausible for the following reasons:

These rays are deflected by electrically-charged bodies. Figure 11 shows the apparatus with which J. J. Thomson proved this. *C* is the cathode and *A* the anode. A slit in the anode and in a disk *B*, beyond, permit a narrow bundle of parallel cathode rays to pass on into the enlarged part of the tube. *D* and *E* are metallic plates with outside connections. The cathode rays pass in a straight line, and produce a fluorescent spot at *F*. If, now, the terminals of *D* and *E* are connected

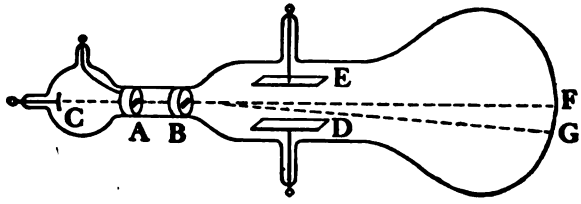


Fig. 11.

with a source of electricity, the plates become charged, and the cathode rays are deflected and produce a fluorescent spot at *G*. The deflection is in the direction indicating that the rays are negatively charged.

Furthermore, we have direct experimental evidence that they carry what we call negative electricity. Figure 12 illustrates the apparatus by which this was demonstrated. *A* is an anode with a hole in it placed opposite the cathode *C*. *B* is a hollow metallic cylinder. The

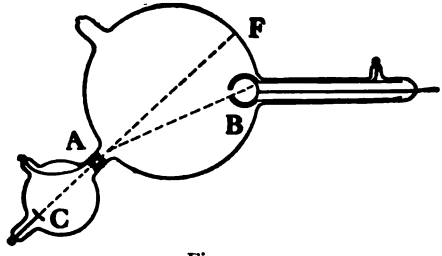


Fig. 12.

cathode rays pass through the hole in the anode and produce fluorescence where they strike the glass in the second bulb at *F*. The cylinder *B* is connected with an electroscope and the electroscope shows no deflection. By means of a magnet the rays are deflected until they enter the hollow cylinder, and then the electroscope shows a deflection and it is found to be negatively charged. This charge must have been brought to the electroscope by the cathode rays.

We are justified then by this evidence in assuming that the cathode rays consist of negatively-charged particles.

Velocity of the Particles. J. J. Thomson estimated the velocity of the particles as follows:* When a particle carrying a charge e moves with the velocity v, and a magnetic force H acts on it at right angles to its line of flight, the force tending to deflect it is equal to Hev. When a particle carrying a charge e passes through an electrical field between plates and the electrical force is X, the force tending to deflect the particle from its line of flight is Xe. In a tube as shown in Fig. 11, he applied such an electrical force as would, alone, cause the fluorescent spot to appear at G instead of at F. He then added a magnetic force acting in the opposite direction until he brought the spot back to F. Then the electric force equals the magnetic force, or $Hev = Xe$, or $v = \frac{X}{H}$, and both X and H may be measured and expressed numerically. He found that in highly evacuated tubes, the cathode rays traveled with a velocity equal to one-third that of light, or about 100 000 kilometers a second. In less highly evacuated tubes, he observed velocities as low as 8300 kilometers a second.

The Value of $\frac{e}{m}$. The value of the ratio of the charge on a particle to the mass of the particle, the value of $\frac{e}{m}$, may be determined as follows:† If a charged particle is flying through an electrical field which exerts a force on it perpendicular to its line of flight, it is like a bullet flying along the earth's surface acted upon by the attraction of gravitation. The distance, S, the bullet will fall in time t is $\frac{1}{2} gt^2$ where g is the gravitation constant. In the case of the charged particle, we have $X\frac{e}{m}$ in place of g, where X, as before, denotes the electric force in the field. The time during which the particle is acted upon by this force is given by $\frac{l}{v}$ where l is the distance covered, and v is the velocity with which it is moving. Substituting in the gravitation formula, we have $S = \frac{1}{2} X \frac{e}{m} \frac{l^2}{v^2}$. In the apparatus sketched in Fig. 11, allow a known electric force to act on cathode rays and measure the displacement of the fluorescent spot, as, for instance, from F to G. This

* "The Corpuscular Theory of Matter," by J. J. Thomson, p. 7.

† *Ibid*, p. 9.

measures the value S; l may be directly measured; we have just seen how v may be calculated; X is known, and so we have numerical values for every term in the expression except $\frac{e}{m}$ and so can calculate its value.

It has been found that the value $\frac{e}{m}$ is a constant quantity, 1.7×10^7 in the C. G. S. system, no matter what the velocity, provided only that it is not almost equal to that of light. This is extraordinary, but it is yet more extraordinary that this value is a constant no matter what the gas in the tube and no matter what the material of the cathode. The particles must come from either gas or cathode, and so it is reasonable to assume that a great variety of substances are capable of putting into existence the same substance, these particles or corpuscles, as they have been named.

Comparison with Hydrogen Ion. The value of $\frac{e}{m}$ for the charged hydrogen ion in solutions is probably about 10^4 in the C. G. S. system, or about $\frac{1}{1700}$ the value of this same ratio for the corpuscle. The mass of the hydrogen ion may be considered to be that of an atom of hydrogen, the lightest item we have ever yet had to consider. Either the charge on a corpuscle must be seventeen hundred times that on a hydrogen ion, or the mass of a corpuscle must be one-seventeen-hundredth the mass of a hydrogen atom. The latter is much the more probable hypothesis for the following reasons:

Charge on a Corpuscle. Upon suddenly expanding a volume of saturated water vapor, it is cooled and a mist forms, each particle of dust present furnishing a nucleus for a particle of mist. Allow time for the mist to settle, carrying down the dust, get the vapor saturated again and again expand. There will be much less fog formed because much less dust is present. By repeating this process, a vessel may be entirely cleared of dust, and no cloud will form as the result of an expansion. Now introduce charged corpuscles and expand and a mist forms. C. T. R. Wilson has shown that each charged corpuscle acts as a nucleus for a particle of mist. If we can count the particles of mist, this will give us the number of charged corpuscles. We can do this.

Stokes' Law. When an object falls, the viscosity of the medium through which it is falling acts like friction to retard the fall. When the object is a very small particle, the force of gravitation is proportionally small, and the surface in contact with the medium is relatively

great. Such a particle soon reaches the maximum velocity it can attain under the circumstances and falls thereafter at a regular, not an accelerated, velocity. Sir George Stokes has formulated this for small spheres in what is known as Stokes' law. If v equals this maximum velocity, a the radius of the sphere, g the gravitation constant, and μ the coefficient of viscosity of the medium, then $v = \frac{2}{9}\frac{ga^2}{\mu}$.

We know the viscosity of air at any temperature, and we can produce a cloud by expansion of saturated water vapor in the presence of charged corpuscles, and observe the rate at which this cloud falls. This gives us v, and substituting in the formula, we calculate the radius of one sphere of mist, and from this its volume. We can calculate the total quantity of water precipitated from the amount of the expansion, and dividing its total volume by the volume of one particle, we obtain the total number of mist particles; *i.e.*, the total number of charged corpuscles. We can measure the total amount of electricity in the gas, and dividing this by the number of charged particles get the charge on one particle.*

The charge is found to be 3.1×10^{-10} electrostatic units, or 10^{-20} electromagnetic units. This is practically the same value as that which has been calculated for the charge on one hydrogen ion in solution.

Mass of a Corpuscle. We have seen that the value of $\frac{e}{m}$ for a corpuscle is 1.7×10^7, while the value of $\frac{e'}{m'}$ for a hydrogen ion in solution is 10^4. Now that we have learned that $e = e'$, it follows that $m' = 1700\,m$, or 1700 of these corpuscles have the same mass as one atom of hydrogen.

Nature of the Anode Rays. As has been said, the anode sends out what are called canal rays. They produce fluorescence where they strike solid bodies, as do cathode rays, but the character of the light is different. When cathode rays strike lithium chloride, a steely blue light is sent out; when canal rays strike the same substance, a brilliant red light is seen.† The canal rays are deflected by a magnet to a less degree than the cathode rays, and in a direction indicating that they are particles charged with positive electricity.

* An experimentally simpler method of counting the particles has been devised by H. A. Wilson. See "The Corpuscular Theory of Matter," by J. J. Thomson, p. 15.

† J. J. Thomson, *loc. cit.*, p. 17.

W. Wien has determined the value of $\frac{e}{m}$ for the canal rays by the methods just described for cathode rays. The values are not constant as for cathode rays, but vary within a rather wide range, and they are all much smaller. The largest yet found is 10^4, from which we are inclined to surmise that the canal rays consist of particles of the size of hydrogen atoms or larger, charged with positive electricity. J. J. Thomson has found, with numerous different gases, that the positively charged particles have values for $\frac{e}{m}$ either 10^4 or one-half this; *i.e.*, we may assume them to contain particles with the mass of the hydrogen atom or of the hydrogen molecule. This is extraordinarily similar to Prout's hypothesis in a new form.

The Nature of X-rays. Where cathode rays strike a solid object, we have a source of X-rays. What the nature of these X-rays may be has been the subject of much study and discussion. The following is a plausible hypothesis: The cathode rays consist of charged particles. A charged particle in motion is surrounded by a magnetic and an electric field of force. These fields may be considered as consisting of systems of Faraday's tubes of force; as it were, filaments of luminiferous ether, some of them in circles, others extending straight outward to infinity. While the corpuscle is moving rapidly, and yet not with the velocity of light, this system of filaments will keep up with it and maintain its position as if rigidly attached. Bring the corpuscle to a sudden stop and the filaments near the corpuscle will stop simultaneously, but the more distant portions of the filaments will continue to move at the old rate. This produces a bend in the filaments, and this bend proceeds outward with the velocity of light rectifying their positions. Thus the suddenly stopped corpuscle becomes the origin of an electric and magnetic disturbance which proceeds outward in a sphere with the velocity of light. J. J. Thomson considers the X-rays to consist of these electromagnetic disturbances.

Let us stop a moment here to summarize the experimental evidence before us. It appears we can get corpuscles one-seventeen-hundredth the probable size of a hydrogen atom, corpuscles the probable size of hydrogen atoms, and twice that size, from a variety of substances, from different gases, and from different metals, and they are the same whatever the gas, whatever the metal. This is certainly strong evidence that atoms are not ultimate particles, and that we are on the

track of something more elementary than our "elements." This hypothesis is corroborated by a large number of facts which we have obtained from the phenomena of radioactivity.

Radioactivity. In 1896, A. H. Becquerel (1852–) discovered that the double sulphate of uranium and potassium sends out rays which pass through black paper, or thin sheets of metals, and affect a photographic plate.* He traced this property to the element uranium, which was therefore called radioactive. He also discovered that these rays, like Röntgen rays, cause gases to become conductors of electricity. This last property is particularly important, as it gives us a marvelously sensitive quantitative method for detecting and measuring radioactivity.

Electroscope. The electroscope is an old and familiar instrument. A simple form is a strip of thin metal, usually gold or aluminium foil, an eighth to a quarter of an inch wide, by one or two inches long, hanging freely over a wire and enclosed in a glass flask, or in a box of any material with windows through which the foil may be observed. The wire carrying the thin strip passes through the case to an outside terminal. Give the instrument a charge of static electricity, for instance, by touching the terminal with a rod of sealing wax recently rubbed with dry flannel, and the two ends of the foil become similarly charged, repel each other, and stand out at an angle from each other. The size of this angle is a measure of the charge. In case the insulation is perfect, this angle remains unaltered for a long time. If the insulation is not perfect, the charge escapes and the ends of the foil approach each other. When a radioactive substance is brought close to, but not touching, the terminal of the instrument, the ends of the foil begin to fall together. Therefore, such bodies do make the air conduct electricity better than it conducted in their absence.

The Most Sensitive Test. This method is the most sensitive known to chemists for detecting the presence of substances. A mere trace of a feebly radioactive substance in the midst of a relatively large mass of indifferent material will affect an electroscope. It considerably exceeds in sensitiveness even our spectroscopic methods, which have hitherto held first place. Moreover, it is quantitative, for doubling the concentration of a radioactive substance in a definite position with relation to an electroscope will double the rate at which the electroscope is discharged. By constantly referring to this in-

* *Compt. Rend.*, **122**, 420, 501, 559, 689, 762, 1086 (1896).

strument, we can tell how we are progressing in efforts to isolate a radioactive substance.

In 1898, G. C. Schmidt* and Madame Sklodowska Curie,† simultaneously and independently, discovered that thorium and its compounds send out rays which discharge an electroscope. These substances are then radioactive. Upon investigation, two minerals of uranium were found which had greater radioactivity than pure uranium. These were pitchblende, so complicated a mineral it may be said to contain a little of almost every known metal, and chalcolite, a phosphate of calcium and uranium. The inference was obvious that these minerals contained an undiscovered substance considerably more radioactive than uranium.

Monsieur and Madame Curie set about the discovery of this new substance endeavoring to isolate it from pitchblende by usual methods of analysis. Having effected a separation they determined the radioactivity of the products with the assistance of an electroscope. With its aid they could tell in which product the radioactive material was, and, after any precipitation or crystallization, could tell that they were nearing their goal if the activity had increased. After they had obtained a product about fifty times as radioactive as their original material they first saw new spectrum lines. This illustrates the statement that the electroscope method of detecting radioactivity much exceeds spectroscopic methods in delicacy.

Polonium. Pitchblende was dissolved in acid and sulphides were precipitated with hydrogen sulphide. The sulphide of bismuth carried a very active material with it. They found that the sulphide of the active substance is more volatile than the sulphide of bismuth, and so effected a separation by sublimation in a vacuum. When nitric acid solutions of the substance with bismuth are diluted, the basic nitrate precipitates, and this is more active than that which remains in solution. When sulphides are reprecipitated from a very acid hydrochloric acid solution with hydrogen sulphide, what precipitates is more active than what remains in solution. Madame Curie called the new substance polonium. It disappears rather rapidly, and is half gone in about six months. It is the first of our new radioactive elements discovered.‡

Radium. The fractions from the analysis of pitchblende contain-

* *Annal. d. Phys.*, **65**, 141–151 (1898).

† *Compt. Rend.*, **126**, 1101–1103 (1898).

‡ Mme. Curie, *Compt. Rend.*, **127**, 175 (1898).

ing barium were also active and, as is well known, the Curies succeeded in isolating practically pure chloride and bromide of the new element which they called radium. The separation from barium compounds depends on the fact that radium chloride or bromide is less soluble in water than barium chloride or bromide. Many fractional crystallizations are necessary, and the quantity of radium in pitchblende is so small that tons of the mineral have to be treated to obtain a few milligrams of radium chloride or bromide.

Madame Curie and A. Debierne* electrolyzed a radium chloride solution using mercury as a cathode. They drove off the mercury by heat in a current of hydrogen and obtained metallic radium. It is a white glistening metal which tarnishes rapidly in the air, decomposes water violently, and melts at 700°. Its symbol weight is 226.4.

Actinium. A. Debierne,† working on pitchblende residues, traced down another radioactive substance, called actinium, which is associated with thorium.

Properties of Rays from Radium. The rays from radium or its compounds cause gases to conduct electricity and affect photographic plates. They produce fluorescence when they strike the zinc sulphide or barium platinocyanide screens used in connection with X-ray work.‡ They color glass and crystals of numerous salts, such as potassium chloride, as do X-rays. They convert oxygen to ozone, and destroy any not very stable organic compounds. They decompose water into its elements; a solution of a radium compound evolves a mixture of oxygen and hydrogen, in not quite the stoicheiometric proportions, slowly but unceasingly. A small amount of hydrogen peroxide is formed simultaneously and this accounts for the deficiency in oxygen.

Nature of the Rays Constituting Radioactivity. Rutherford has distinguished three kinds of rays "by observing whether the rays are appreciably deflected in a magnetic field" and "by comparing the relative absorption of the rays by solids and gases." He calls them α-, β-, and γ-rays. Following is his description of them:

* *Compt. Rend.*, 151, 523 (1910). Also *Nature*, 84, 313, 356, 478 (1910).

† *Compt. Rend.*, 129, 593 (1899), and 130, 206 (1900).

‡ **Spinthariscope.** An interesting little instrument called a spinthariscope is obtainable at small cost. A fragment of not particularly active material is mounted a short distance above a coating of zinc sulphide within a metallic tube. Looking through a lens in one end of the tube, brilliant scintillations are seen as the rays strike the screen.

(I) The α-rays are very readily absorbed by thin metal foil and by a few centimeters of air. They have been shown to consist of positively-charged bodies projected with a velocity of about one-tenth the velocity of light. They are deflected by intense magnetic and electric fields, but the amount of deviation is minute in comparison with the deviation, under the same conditions, of the cathode rays produced in a vacuum tube.

(II) The β-rays are far more penetrating in character than the α-rays, and consist of negatively-charged bodies projected with velocities of the same order as the velocity of light. They are far more readily deflected than the α-rays, and are in fact identical with the cathode rays produced in a vacuum tube.

(III) The γ-rays are extremely penetrating, and nondeviable by a magnetic field. Their true nature is not definitely settled, but they are analogous in most respects to very penetrating Röntgen rays.*

The α-rays correspond to the canal or anode rays, the β-rays to the cathode rays, and the γ-rays closely resemble the X- (or Röntgen) rays, but have more power of penetration.

Figure 13 is a diagram first used by Madame Curie to illustrate the difference between these rays. A radium compound is placed in the bottom of a lead tube on a photographic plate. A strong magnetic field is applied at right angles to the plane of the paper and downwards. β-rays are much deflected in the sense indicating they are charged with negative electricity. α-rays are less deflected than appears in the figure, in the sense indicating they are charged with positive electricity. γ-rays are not deflected.

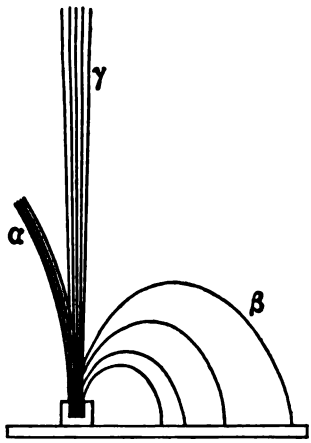


Fig. 13.

Evolution of Helium. In 1903, Ramsay and Soddy proved that radium compounds evolve helium continuously. Rutherford and Boltwood have found that helium is produced from radium compounds at the rate of 163 cubic millimeters per gram radium per year, and also proved that polonium evolves helium.† Extraordinary as the fact is, it must be accepted, for the observations have been made many times by several independent investigators. One element is actually changing into an-

* "Radioactivity," by E. Rutherford, second edition, p. 109 (1905).

† E. Rutherford and B. B. Boltwood, *Manchester Lit. and Phil. Soc. Mem.*, **54**, 1-2 (1909-1910).

other. This is an exceptionally important fact, for it is the first instance of the kind definitely established.

Occasionally, claims have been advanced that one element could change to another, but they have not been verified by subsequent independent investigators. For instance, it was claimed in 1889 that tubes in which chlorine, and others in which iodine, had been sealed up for eight or ten years showed the chlorine or iodine spectrum with slowly diminishing distinctness, while the hydrogen spectrum appeared faintly at first, but with gradually increasing distinctness.* These observations have not been verified, and cannot be accepted with the confidence we may legitimately feel in these changes of radioactive substances.

Ramsay recently thought that lithium and potassium could be obtained from a salt of copper subjected to the influence of the radiations from radium, but Madame Curie could not duplicate his results. It is then an open question, and a particularly important one, for though we may consider it as settled that the radioactive substances undergo these changes themselves, it would be a much more wonderful advance if we could cause them to produce analogous changes in other substances.

New Elements. Rutherford has demonstrated that not only helium but also several entirely new substances, with properties so distinct he believes them to be hitherto undiscovered elements, put in an appearance, one after the other, as a result of the radiation from radium compounds; apparently intermediate products between radium and some end product about which we are not yet certain.

The amount of radium disappearing while these new substances are being evolved is small, too small to measure by any ordinary analytical method. But the intensity of radiation (rate of discharge of an electroscope) is a measure of the amount of radioactive substance present, and this makes it possible to form estimates, though these estimates sometimes differ rather widely. For instance, Rutherford says half of any original quantity of radium will have disappeared at the end of 1300 years, while Debierne is unwilling to accept so definite a time, and says it may be anywhere between 250 and 2000 years.

Application of Law of Mass Action. The law of mass action appears to apply to the rate at which a radioactive substance disappears in the form in which it applies to monomolecular chemical

* See footnote in Preston's "Theory of Heat," pp. 62–63, and *Nature*, 40, 584 (1889).

reactions. For instance, starting with four milligrams of radium, we should find it half gone after 1300 years, and two milligrams would be left. It would take another 1300 years for half of what was left to disappear, leaving one milligram; a third like period to halve our supply again, and so on to eternity.

Half Period. The rate at which it disappears is one of the most characteristic properties of a radioactive substance. It has, therefore, been adopted as a convenient numerical property. We speak of the "half period," by which we mean the time required for one-half of any original amount to disappear.

Fixed Proportions of Uranium and Radium. A number of minerals containing uranium have been found to contain radium in a fixed proportion. This is plausibly explained by assuming that uranium is slowly disappearing and changing into radium. Radium disappears also, and in the course of time an equilibrium establishes itself, such that the amount of radium formed from uranium per unit time just equals the amount which disappears.

Range of α-Rays. It has been found that the α-rays from a radioactive substance do not go far, only a few centimeters in air, and what we may call their "range" may be measured; again by means of an electroscope.

Rutherford's Table. Following is a table which contains a series of the products due to the disintegration of radioactive elements, their half periods, a property by which each may be characterized, nature of the rays sent out by each, and range of α-rays, the whole based on Rutherford's table with a few minor additions from other sources.

	Symbol weight.	Half period.	Properties.	Nature of rays.	Range of α-rays.
Uranium...	240	5.10^8 years (5.10^9 years)	The nitrate is soluble in ether.	α	3.3 cm.
Uranium X.	.....	22 days	Nitrate difficulty soluble in ether.	β, γ	.....
Radium....	226.4	1300 years (250–3000 years)	Like barium.	α, β	3.5 cm.
Radium α.. (Niton)..	(222.4)	4 days	"Noble gas" condenses to a liquid at $-150°$.	α	4.23 cm.
RA.....	(218.4)	3 minutes	Difficult to volatilize	α	4.83 cm.
RB.....	(214.4)	26–28 minutes	Difficult to volatilize	Inactive or very slow β rays.	.....
RC.....	(214.4)	19 minutes.	Separable by electrolysis.	α, β, γ	7.06 cm.
RD.....	(210.4)	About 40 years?	Separable by electrolysis.	Inactive	.....
RE.....	(210.4)	6 days	Separable by electrolysis.	β, γ	.....
RF.....	(210.4)	140 days	Separable by electrolysis.	α	3.86 cm.

A similar table has been constructed for the disintegration products from thorium, but it is hardly desirable to include it as these tables cannot as yet be considered as finished. New facts are constantly being discovered and old ones modified or revised. One such table illustrates adequately the points of immediate importance for us.

Is Radium an Element? It may be thought odd that, knowing it splits up into simpler substances, we should call radium an element, but, besides the fact that it has a definite spectrum not obtainable from any other known substance, we have learned things about it which make it more logical to modify our old ideas regarding elements than to exclude radium.

Evolution of Heat. Radium compounds evolve heat continuously at a definite rate. From measurements in calorimeters, it has been possible to determine that one gram of pure radium evolves one hundred small calories an hour, and this evolution continues at the same rate, no matter what the particular compound in which the radium is, no matter whether it is at the temperature of liquid air or heated to 1300° in an electric furnace,* no matter whether it is solid or in solution. This is very extraordinary, and conclusive evidence that whatever it is which is going on and which manifests itself in these radiations, it is not like any other known chemical process. For no previously known chemical process proceeds at a definite rate regardless of temperature and of the conditions of aggregation of the substances involved. We have here, manifestly, an entirely new sort of process, and the only plausible hypothesis as yet suggested is that these phenomena are obtained solely when elements disintegrate.

From these figures it has been calculated that the disintegration of one gram of radium develops at least one hundred thousand times as much heat as can be obtained by burning one gram of carbon. We may safely say the energy involved is many thousand times greater than that involved in the most violent chemical reaction previously measured.†

We are dealing here with greater concentrations of energy than ever

* H. W. Schmidt and P. Cermak, *Phys. Zeitschr.*, 9, 816–821 (1908), and 11, 793–800 (1910), found a difference in amount of radiation not exceeding 5 per cent at this high temperature.

† Whetham, assuming several steps in the disintegration and this large evolution of heat at each step, says: "The energy liberated by a given amount of radioactive change . . . is at least 500 000 times, and may be 10 000 000 times, greater than that involved in the most energetic chemical action known." — "The Recent Development of Physical Science," p. 229. (1906).

before observed, and this is a strong argument in favor of the view that we are for the first time observing the splitting up of an element into simpler substances.

Heat of the Earth. It has been the subject of some speculation why the earth and sun do not cool off faster than they do, and various hypotheses have been suggested. The most recent idea is that the source of the heat may be the disintegration of these radioactive elements. It is possible to estimate the amount of radioactive material in the earth's crust, and the surprising result has been reached that not only is the slowness of cooling accounted for, but this earth ought to be growing warmer all the time. We have overshot the mark, but these calculations are subject to revision, and we need not fear an immediate and oppressive change of climate.

The Rutherford-Soddy Hypothesis. Rutherford and Soddy have advanced the hypothesis that atoms consist of many small particles revolving with great velocities, and that occasionally one particle flies off. When this happens we observe radioactivity; *i.e.*, rays consisting of particles. α-rays they consider as atoms of helium. β-rays are probably corpuscles like those constituting cathode rays. γ-rays are probably like X-rays, electromagnetic disturbances resulting from the sudden stopping of β-rays which start in the interior and impinge on another portion of the radioactive substance nearer its surface.

δ Rays. To the three kinds of rays previously described, perhaps a fourth kind should be added, called δ-rays. These are probably negatively charged particles of the same order of magnitude as the positively charged α-ray particles, readily deflected by a magnet in the same direction as the β-rays, having relatively low velocities and particularly easily absorbed.

End Product of Disintegration. Now if α-rays consist of atoms of helium, and if we further hypothecate that one atom of radium loses one atom of helium, since the atomic weight of helium is four, what is left, or niton, should have an atomic weight of $226.4 - 4$ or 222.4. Apply this hypothesis through the series, and we obtain the probable atomic weights in parentheses in the table. Since *RB* does not send out α-rays, it and *RC* should have the same atomic weight. *RF* sends out α-rays; therefore the next member of the series should have an atomic weight of 206.4. This is the symbol weight of lead, and thus Rutherford reaches the conclusion that lead is probably the end product of the disintegration of radium. This has not been verified,

and none of the intermediate atomic weights have been determined; therefore, judgment should be suspended.

Other Radioactive Substances. Lead has been found to be radioactive, but the experimental results cannot be said to have added weight to this hypothesis. Potassium is also radioactive, and numerous other substances have been found to be more or less feebly radioactive.

Induced Radioactivity. This difficulty attaches to the search for traces of the property; any substance, exposed to a source of radioactivity becomes itself a source of radioactivity. This is called "induced radioactivity." It has been found to be due to the gas niton, called emanation by Rutherford, which condenses on surfaces.

Stability of Elements. If many α particles are shot out in unit time, that "element" may be considered as a rather unstable compound; if few, it may be considered as rather stable. Our experience is mainly with the latter, for the former must have lived their lives in the past and have long since ceased to exist. As was suggested in Chapter VII, perhaps these are the elements which would fit into the vacant spaces of the periodic system.

The experimental evidence from cathode, anode, and X-rays, from α-, β-, and γ-rays, all alike no matter what their source, is making it more and more plausible to consider our elements as compounds, our atoms as highly complicated systems of particles in extremely rapid motion.

Sir Oliver Lodge has suggested that the atoms of chemistry may be looked upon as solar systems of corpuscles, revolving about each other in definite orbits, with interstitial spaces between the different corpuscles as great, with reference to the size of one, as the distances in our solar system are to the sizes of the sun and planets. According to this, substances may be considered as owing their special properties to the number of corpuscles in the unit of the substance as such (the atom) to their velocities, and to the particular orbits they describe. If we consider all differences between substances as due to different combinations of one thing, we arrive at a sort of revised edition of Prout's hypothesis once more. It is strange how that underlying idea of one fundamental substance will not stay buried.

Absorption of Rays. P. Lenard* has shown that the absorption of cathode rays by different substances is simply proportional to the specific gravity of those substances and independent of their chemical properties. It is even independent of the condition of aggregation;

* *Wied. Annal.*, **56**, 255 (1895), and *Drudes Annal.*, **12**, 714 (1903).

i.e., whether the absorbing substance be a gas, a liquid, or a solid. This is another argument in favor of the view that all substances consist of the same ultimate constituent, probably what we mean when we speak of corpuscles. Then corpuscles must be considered as passing unimpeded through the interstices between the corpuscles of the atom.

Dynamides. Lenard calls the corpuscles dynamides, and considers them as fields of electrical force with impenetrable central bodies which then constitute actual matter. He calculated the diameter of this center of actual matter as smaller than 0.3×10^{-10} mm. (0.000 000 000 03 mm.). Applying these results to platinum, one of the most dense of the metals, one of those with the highest specific gravity, he concludes that a solid cubic meter of platinum is in truth an empty space, with the exception of, at the outside, one cubic millimeter occupied by the actual matter of the dynamides.

If we can thus reasonably and mathematically so nearly eliminate the matter of a cubic meter of one of our densest metals, it should not be very difficult to make one more effort and eliminate that insignificant little cubic millimeter still remaining.

Apparent Mass Due to Electric Charge. An electrically charged body moving with a high velocity, has an apparent mass greater than its normal mass, the excess being due to the electrical charge in motion.

A measure of the mass of a body is its inertia. The work which must be done upon it to set it in motion at a certain rate is equal to the kinetic energy which it has after a force has done its work, or $\frac{1}{2} mv^2$. When an electrically charged body is moved, it produces a magnetic force around itself, and this is a form of energy added to the kinetic energy. Energy cannot be created; therefore this additional energy must come also from the force doing the moving. In other words, more work must be done to move a body when electrically charged than when not so charged. If W represents the work required to move the mass, and W' the work required to move the charge, we must do $W + W'$ work to set the system in motion. W' is so small with ordinary objects as not to be detectable, but the smaller the mass and the greater the charge and the greater the velocity of the motion, the greater is W' as compared to W. Applying this reasoning to the corpuscles, it may be calculated that when their velocity nearly equals that of light, W' becomes so large as compared to W that the latter practically vanishes; *i.e.*, all the work consists in moving the charge,

and the mass in the ordinary sense of the word vanishes, or better, the observed mass is nothing but electricity in motion. This reasoning is relatively old, but it has not been possible to put it to an experimental test until recently.*

Kaufmann's Results. Radium sends out corpuscles which travel at different velocities, some relatively slowly, others with speeds approaching that of light. Those going fastest should have the greatest apparent masses. W. Kaufmann† has determined the value of the ratio $\frac{e}{m}$ for these different corpuscles experimentally by the methods outlined in the earlier part of this chapter. From these values, he calculated the masses of the rapidly moving corpuscles and compared them with the mass of a corpuscle moving so slowly that W' is insignificant as compared to W. His results are contained in the second column of the following table. The first column contains the velocities. The third column contains the values which should have been obtained if the observed mass is ascribable wholly to electricity in motion.

Velocity.	Mass found. (Mass of slow corpuscle = 1).	Mass calculated on this hypothesis.
2.85×10^{10} cm./sec.	3.09	3.1
2.72×10^{10} cm./sec.	2.43	2.42
2.59×10^{10} cm./sec.	2.04	2.0
2.48×10^{10} cm./sec.	1.83	1.66
2.36×10^{10} cm./sec.	1.65	1.5*

* Values taken from J. J. Thomson. "Corpuscular Theory of Matter," p. 33.

The correspondence is surprising and justifies us in assuming that the whole mass of the corpuscle is due to electricity in motion.

* This idea may seem strange when first presented, but it does not transcend all experience. We have all watched with interest a spinning gyroscope supported only at one end of a horizontal axis and apparently defying the laws of gravitation. We know it does not fall because it requires a notable force to alter the plane of the spinning motion. We formulate this behavior in the first law of motion, which of course formulates only and does not explain. But the hypotheses we are considering also formulate only and contain no ultimate explanation. It may be of some help to liken an atom to a gyroscope, and to think of it as having inertia; *i.e.*, mass, because a force is required to alter the direction of motion of the constituent corpuscles.

† *Gesell. Wiss. Göttingen, Nachr., Math.-Phys. Klasse*, 5, 219–296 (1902).

Thomson says: "These results support the view that the whole mass of these electrified particles arises from their charge." *

Electron. The corpuscle then contains no kernel of "matter," hard and unyielding, a "carrier" of energy; it is simply an electric charge in motion. The term electron was substituted by Stoney for the term charged corpuscle, to indicate in the name itself the electrical nature of these ultimates of our present knowledge.

We have found numerous reasons for thinking that an atom consists of a complicated system of electrons moving in orbits with velocities approaching that of light. We may then say, as the mass of each electron is merely a manifestation of electricity in motion, the atom as a whole owes what we call its mass to electrical charges in motion, and if the atom, then the molecule and all aggregations of molecules and, in short, every body, object, substance, thing in the objective universe consists of complicated systems of electrical charges in rapid motion. The concept, matter, becomes superfluous as the property, mass, is more logically accounted for, and the universe we study becomes a universe of energy in motion. This may appear to some readers an extreme view and distasteful, but it is certainly logical and when its novelty has worn off a little, it will be found more acceptable, because more reasonable than any other hypothesis yet suggested regarding the ultimate constituents.

Atoms. Notice that this does not eliminate the concept atom at all. On the contrary, it describes it in greater detail and lends it a reality it never before possessed. Our atoms can no longer be thought of as ultimates and indivisible, but must be imagined as highly complex compounds, distinguished from all other compounds by their extreme stability, a stability not destroyed by the forces we can control, unless the electrodes in Röntgen tubes can be demonstrated to be undergoing a disintegration, like uranium, thorium, or radium. Our atoms still remain in our thoughts the units of our so-called elements, though not the ultimate units, and we may still consider ordinary chemical processes, with the aid of our old and useful mechanical model, the atomic theory.

Electron Theory Offers Plausible Explanations. The adoption of this electron theory furnishes us with a plausible explanation of many facts. For instance, we may think of valence as follows: An atom less one electron, or plus one electron, may be considered as electrically charged, and therefore capable of attracting other bodies,

* "Electricity and Matter," p. 48.

equally and oppositely charged, to form electrically neutral systems. An atom less two electrons, or with two electrons in excess, would have twice the capacity for combination, it would be what we call bivalent, and so on. Again, an electronic structure of the atom furnishes a plausible explanation of the rotation of the plane of polarized light. Hitherto, the customary cause and effect connection between the explanation and the fact has been entirely lacking. Granting the actual objective existence of tetrahedral carbon atoms, with different groups asymmetrically arranged at the apices, the question still remains, why should such a structure be able to rotate the plane of polarized light? Grant that the molecule consists of systems of charged corpuscles traveling in well-defined orbits, with velocities approaching that of light, and we can see that light, consisting of electromagnetic disturbances, traversing this maze, *must* be influenced.

Faraday's Opinion. Michael Faraday is acknowledged to have been one of the ablest of experimenters and clearest of thinkers. It is therefore of present interest to notice what his opinions were regarding the ultimate constituents. In an article published in 1844, he says:

> If we must assume at all, as indeed in a branch of knowledge like the present we can hardly help it, then the safest course appears to be to assume as little as possible, and in that respect the atoms of Boscovich appear to me to have a great advantage over the more usual notion. His atoms, if I understand aright, are mere centers of forces or powers, not particles of matter, in which the powers themselves reside. If, in the ordinary view of atoms, we call the particle of matter away from the powers *a*, and the system of powers or forces in and around it *m*, then in Boscovich's theory *a* disappears, or is a mere mathematical point, whilst in the usual notion it is a little unchangeable, impenetrable piece of matter, and *m* is an atmosphere of force grouped around it. . . . To my mind, therefore, the *a* or nucleus vanishes, and the substance consists of the powers or *m*; and indeed what notion can we form of the nucleus independent of its powers? All our perception and knowledge of the atom, and even our fancy, is limited to ideas of its powers; what thought remains on which to hang the imagination of an *a* independent of the acknowledged forces? A mind just entering on the subject may consider it difficult to think of the powers of matter independent of a separate something to be called *the matter*, but it is certainly far more difficult, and indeed impossible, to think of or imagine that *matter* independent of the powers. Now the powers we know and recognize in every phenomenon of the creation, the abstract matter in none; why then assume the existence of that of which we are ignorant, which we cannot conceive, and for which there is no philosophical necessity?*

* "Experimental Researches in Electricity," by Michael Faraday, Vol. 2, pp. 289–91.

We have reached the frontier of our science in its search for the ultimate constituents.

Summary. Spectroscopic evidence leads us to believe that at the higher temperatures, lower pressures, and different electrical conditions which seem to prevail on some stars, our elements are dissociated to simpler substances, perhaps one substance, and that with descending temperatures elements with larger symbol weights are formed by a process of inorganic evolution.

Radioactive evidence leads us to believe that elements with large symbol weights are dissociating and giving those with small symbol weights, and evolving immense quantities of heat in the process.

It seems as though we were gradually learning about segments of a great cycle, but many segments are missing, and we are far from understanding the cycle as a whole.

What we observe and measure is always and exclusively heat, light and electricity. These are essentially the same thing, vibrations, differing only in wave length. They may then be considered as one form of energy. We reach an astonishingly simple result. All we observe is energy. All energy is motion. The time appears to be approaching when we shall be able to formulate mathematically every substance and every process in terms of motion; that is, in ratios between time and space.

SECTION III

PROPERTIES

CHAPTER XI

GASES

THUS far we have been engaged primarily with the efforts to answer the question, what are the ultimate constituents? We have found it rather comprehensive and not finally answerable. In the next nine chapters we shall consider in some detail certain properties characteristic of the several conditions of aggregation. This is the customary plan, but we shall modify it slightly, reserving the consideration of all processes, so far as possible, for the last eleven chapters.

The definition of a gas and the gas laws have been given in Chapter III, and need not be repeated. We shall now take up the kinetic theory of gases as all necessary preliminary facts have been presented.

Kinetic Theory of Gases. Chemists, starting from the hypothetical unit, the atom, found it necessary, as we have seen, to assume the existence of aggregates of two or more atoms to form molecules. They further found it desirable, if not necessary, to form a definite picture of the structure of a gas, and so adopted Avogadro's theory. This really contains the most fundamental assumption of the kinetic theory of gases, namely, that they consist of discrete particles, conveniently called molecules. Other facts, more physical than chemical, led to the elaboration of the theory. This is one of the many instances where the two sciences meet and merge, instances which are so frequent that no adequate knowledge of either subject can be had without a reasonable acquaintance with the main facts and theories of the other.

Earliest Suggestions. Daniel Bernoulli (1700–1782), in 1738, suggested essentially the same theory we have since adopted.* J. J.

* D. Bernoulli, (sometimes spelled Bernouilli), "Hydrodynamica" (1738).

Waterston presented the hypothesis to the Royal Society in London, in 1845, but his paper was not published, the editors evidently not appreciating its worth. Lord Rayleigh discovered it in the archives and caused it to be published in 1892.* Kroenig, Clausius, Maxwell, Boltzmann, O. E. Meyer, and van der Waals are most prominently associated with its development.

We shall approach the subject inductively, stating experimental facts first and then suggesting plausible explanations for them.

Spectrum. A gas absorbs light of definite wave lengths. The absorption must be due to the substance of the gas, because the dark lines are the same whether the gas is under a low pressure and occupying a large volume, or under a high pressure and occupying a small volume. Therefore the substance of the gas, the matter, if you will, does not change when the volume changes. A plausible explanation for this is that a gas consists of small discrete particles, at a distance from each other with space between them. For then an increase in volume implies an increase in the space and no change in the particles themselves.

Transmission of Odors. A gas, liberated in an empty vessel, fills that vessel homogeneously, or an odor, liberated at one place in a room, soon fills the room. A heavy gas, like bromine, liberated at the bottom of a cylinder filled with a lighter gas, like hydrogen, diffuses upward, against the attraction of gravitation, until the cylinder is homogeneously filled. A plausible explanation for these facts is that the discrete particles of the gas are in motion.

A gas, liberated in a vacuum, fills that vacuum practically instantly. Therefore we must assume the motion of the particles to be very rapid. They must be some distance apart, otherwise the attraction which we must assume they exert on each other would hold them together and prevent them from thus filling any containing vessel.

Cannot Separate by Diffusion. A gas which is a chemical individual (not a mixture) cannot be separated by diffusion through porcelain, or any other known membrane with fine openings, into two portions, one portion able to diffuse more rapidly than the other in a subsequent experiment. If there were any difference in the sizes of the discrete particles, we should doubtless succeed in finding an appropriate membrane and effecting such separation into portions diffus-

* Waterston's memoir, entitled "On the Physics of Media that Are Composed of Free and Perfectly Elastic Molecules in a State of Motion," was received December 11, 1845. It was published in *Phil. Trans.*, **183**, 1 (1892).

ing with different rapidities. A plausible explanation for our failure to accomplish this is that all the particles are the same in size and weight.

Pressure. Gases exert pressures on the sides of containing vessels. We can think of no other explanation for this than that gases consist of particles in motion which hit the sides, and the sum of all the impacts is the pressure we observe. The particles must also hit each other.

Elasticity. If the particles hit each other or the sides of the vessel and rebounded with less velocity than they had originally, after enough contacts they would come to rest and would lose their property of filling any vessel completely. But a gas does not lose this property upon standing and the pressure does not diminish in case the temperature remains the same, so the particles must be imagined as rebounding with undiminished velocities, that is, they must be imagined as perfectly elastic. The walls of the containing vessels must also be considered as perfectly elastic. This is a reasonable enough supposition when we consider the excessively minute deformations which would be produced by such small impacts.

Formulation. Starting from the assumptions which we have reached by this reasoning, it is possible to develop an interesting formula. Different molecules in one gas doubtless have different velocities, but there must be an average velocity. Let c equal this average velocity of a molecule, the distance covered in unit time. Let m equal the mass of one molecule. Consider a cube the length of any edge of which is l. Imagine one molecule moving back and forth perpendicularly to one pair of sides. It hits one side with a force cm, and rebounds with undiminished velocity. (The same velocity with opposite sign.) So the pressure exerted on one side due to one impact is $2\,cm$. The number of impacts in unit time is $\frac{c}{l}$. The pressure is then $2\,mc$ multiplied by the number of impacts, or $\frac{2\,mc^2}{l}$.

If the direction is not perpendicular to any pair of sides it may be resolved by the parallelogram of forces into three components, each of which will be perpendicular to one pair of sides. Let u, v, and w be these components, then the pressure is $\frac{2\,mu^2}{l} + \frac{2\,mv^2}{l} + \frac{2\,mw^2}{l}$. But $u^2 + v^2 + w^2 = c^2$, a well-known proposition of solid geometry.

Therefore $\frac{2\,mc^2}{l}$ holds for the pressure exerted by one molecule no matter what its direction.

Let n = the number of molecules, then $\frac{2\,mnc^2}{l}$ = the total pressure. A cube has six sides so one-sixth of the pressure falls on a side. When we measure the pressure of a gas with a barometer or gauge of any kind we are measuring this pressure which falls on one side. We denote it by p, and therefore $p = \frac{1}{3}\frac{mnc^2}{l}$.

The volume of a cube is the length of an edge raised to the third power or, for our cube, l^3. We may consider we took a cube of edge equal to unity. One, raised to the third power, is one, $l = l^3$, therefore $l = v$, or $p = \frac{1}{3}\frac{mnc^2}{v}$, or $pv = \frac{1}{3}mnc^2$.

Extending the Formula to any Vessel. The formula applies to any body of gas, whatever its size or shape, for we may consider any volume made up of many small cubes. For each cube the formula will hold, and it will hold for the whole volume occupied by all the cubes, for the pressures on the adjacent sides of any two cubes are equal and opposite and so balance each other; therefore the side or division may be considered as not there. The smaller the cubes the more nearly they fill the vessel until, if they are infinitesimally small, they fill the vessel completely. Consequently the formula must hold for any vessel whatever.

Heat a Mode of Molecular Motion. If we alter the temperature of a gas we know that the value pv is altered. If pv alters, so must $\frac{1}{3}mnc^2$ alter in the same measure. But m, the mass of one molecule, cannot be imagined as altering, nor can n, the number of molecules. Therefore the average velocity, c, the only term left, must alter, and the square of the average velocity appears to be a measure of the temperature.

These considerations gave rise to our present idea that heat is a mode of molecular motion. Besides this translatory motion just formulated we imagine the discrete particles, the molecules, to have motion of rotation about their axes and also we imagine the atoms within the molecules to have some sort of motion with respect to each other.

The Absolute Zero. When c equals zero, the product pv must equal zero and we have the absolute zero of our temperature scale

which we reached graphically in Chapter III. At this temperature we must imagine that the molecules no longer fly about. Notice that if we assume p equals zero when c equals zero, the product pv becomes zero and yet the volume v may have any value whatever.

The first suggestion of such a point as an absolute zero was made by Amonton in 1702. His results would have given $-240°$ on the centigrade scale. Lambert utilized Amonton's results, but from his own more careful experiments concluded that the point was at $-270°$. By extrapolation from the gas laws we are led to adopt $-273°$ although all gases first liquefy, then solidify, and the gas laws do not apply. Assuredly the volume would not become equal to zero, and it is easier to think of the pressure falling to zero.

Conductivity of Metals. Pure elementary metals offer less resistance to the passage of electrical energy the colder they are. If we plot the resistance as a function of the temperature on a coördinate system, laying off temperatures on the horizontal and resistance on the vertical, we obtain for each pure metallic element nearly a straight line. While these lines are distributed much like the ribs of a fan through the space, the general tendency of them all is to point to a position on the horizontal axis somewhere near $-273°$ on the centigrade scale. In other words, the resistance of these metals would apparently become equal to zero if they were brought to the absolute zero.

This is a rather rough approximation, for plotting actual experiments as described it would appear as though copper should have a resistance of zero at $-223°$ and yet at the boiling point of liquid hydrogen, $-252.5°$, it still has 1 per cent of the resistance it has at 0°. At $-252.5°$ gold and platinum have 3 per cent, silver 4 per cent, and iron 12 per cent of the resistance they have at 0°.*

Thermodynamic Method. In 1848 Lord Kelvin applied the thermodynamic principles, namely, that a perfect engine should give the same amount of work on any part of the scale when the difference in temperature between the boiler and the condenser is one degree, and that when the condenser is at absolute zero all heat passing through the machine must be converted to work, to an absolute method of temperature measurement independent of the properties of any particular substance. He reached the conclusion that there is an absolute zero at $-273°$.

* Sir James Dewar. Presidential address at Belfast (1902). Reprinted in *Science*, October 3, 10, and 17, 1902.

This conclusion, based as it is then on three different and independent lines of reasoning, on the behavior of gases, on the conductivity of metals, and on thermodynamics, justifies Dewar in saying "the existence of a definite zero of temperature must be acknowledged as a fundamental scientific fact."

Heat Motion is not Electron Motion. We may consider the absolute zero as the point where all that sort of motion which we appreciate as heat has ceased; but this is by no means all the sorts of motion which we can imagine. We have good reason to assume that there is much motion within a molecule, and within an atom also, which is not evident as heat. Our conception of conditions at the absolute zero leaves such motions wholly out of consideration.

Interstellar Space. There is little if any probability that we shall ever reach the absolute zero, each further step is so much harder than that preceding. An object in interstellar space, and very transparent to radiant energy, would doubtless be above the absolute zero, owing to the fact that it would intercept the sun's or stars' rays and convert them to heat.

Chemical Action at Low Temperatures. The great majority of chemical actions are suspended at extremely low temperatures, but others still occur. At $-80°$ alcohol containing water no longer acts on metallic sodium, but fluorine is still active at the temperature of liquid air.

Density. Bodies become denser the lower the temperature, but ice, which of course occupies a larger volume than the same weight of water at $0°$, although it increases in density as the temperature falls, does not reach the density of water at $0°$ even at the lowest temperature at which it has been measured. This shows that substances do not necessarily occupy the smallest possible volume.

A theory, to be accepted as useful, must enable us to deduce known facts and new facts. The kinetic theory of gases certainly fulfills the requirement, for we can easily deduce from it the gas laws and Avogadro's hypothesis.

Deduction of Boyle's Law. In the formula, $\frac{1}{3} mnc^2 = pv$, all the terms on the left of the equality mark are constant values if the temperature be held constant. Then we may read pv = a constant, and this is the best expression of Boyle's law.

Deduction of Gay-Lussac's Law. The kinetic energy of a moving body is one-half the product of the mass into the square of the velocity. We may write our formula, $\frac{2}{3} \frac{nmc^2}{2} = pv$. $\frac{nmc^2}{2}$ is the total

kinetic energy of the moving particles and $\frac{mc^2}{2}$ is the average kinetic energy of one molecule.

If we mix two gases at the same temperature and pressure we get no change in temperature or pressure. Maxwell and Boltzmann have shown that if two systems of moving particles have no effect on each other, the individual moving masses must have the same average kinetic energies. We may picture this to ourselves and realize it must be so. Imagine a lot of little globules flying about in a space; add others of the same weight but with greater velocities, and through collisions there will evidently be a change and increase in their average velocity. Add globules of greater weight but with the same velocities and once more the average kinetic energy of the globules must be increased. Thus we can see that there will be no change only when the average kinetic energies are the same. And so, if m_1 and c_1 refer to one gas and m_2 and c_2 to the other, $\frac{m_1c_1^2}{2} = \frac{m_2c_2^2}{2}$.

Do another experiment, raising the temperature of both gases the same amount. This increases both kinetic energies, as c is the only thing which can change. Now mix them at this higher temperature. Once more no effect is produced on either temperature or pressure. That is, the average kinetic energies are still equal to each other, and so the kinetic energies in the two gases must have increased to the same amount. If they have increased to the same amount in both cases, then the value pv must also have increased to the same amount in both cases. But this is the most general statement of Gay-Lussac's law; namely, that equal changes in temperature produce equal changes in the product pv for all gases, and so we have deduced the second gas law from this theory.

Deduction of Avogadro's Theory. Let us take equal volumes of two gases under the same conditions of temperature and pressure. Then p_1v_1, the product of the pressure into the volume for the first gas, equals p_2v_2, the product of the pressure into the volume for the second. Then $\frac{2}{3} n_1 \frac{m_1c_1^2}{2} = \frac{2}{3} n_2 \frac{m_2c_2^2}{2}$. We have just seen that the average kinetic energies of the individual particles in the two gases must be the same since we may mix them without observing any change in temperature or pressure. Therefore, $\frac{m_1c_1^2}{2} = \frac{m_2c_2^2}{2}$, and these terms cancel, as, of course, the fraction $\frac{2}{3}$ does also. We thus have left, $n_1 = n_2$, which is Avogadro's theory.

Velocity of Diffusion of Gases. We may make another deduction from the theory which harmonizes excellently with experimental facts. Since $\frac{m_1 c_1^2}{2} = \frac{m_2 c_2^2}{2}$ for any two gases at the same temperature, $\frac{m_1}{m_2} = \frac{c_2^2}{c_1^2}$ or, $\frac{c_2}{c_1} = \sqrt{\frac{m_1}{m_2}}$. Bunsen based a method for determining molecular weights upon this. We cannot measure directly the absolute velocities of individual molecules, but it is reasonably safe to assume that a gas whose molecules have the greater average velocity will pass through a fine capillary opening, or through the pores of unglazed porcelain or the like, more rapidly than a gas whose molecules have a less average velocity. We may assume that the time required for a given volume of a gas to pass through such a capillary structure is inversely proportional to the average velocity of the molecules. If t_1 and t_2 represent the times required for equal volumes of two gases at the same temperature to get through the same opening, then $c_1 : c_2 = t_2 : t_1$. Substituting in our last equation we have $\frac{t_1}{t_2} = \sqrt{\frac{m_1}{m_2}}$. If we know the molecular weight of one gas we may calculate the molecular weight of the second, and actual experiments give results which agree well with those obtained by other, wholly independent, methods.

That the rapidity with which a gas can pass through a narrow opening is inversely proportional to the square root of its density is the result of a general mechanical consideration, and entirely free from any hypothesis regarding the structure of the gas. That this may be deduced from the kinetic theory is a strong argument in favor of the theory.

Fractional Diffusion. This principle is frequently utilized to separate two gases of different densities. For instance, Ramsay separated the rare elements of the atmosphere, argon, helium, neon, krypton, and xenon, by passing the mixture through a series of pipestems and collecting the gases which diffused through their walls.

Of course this is not an absolute method, and some of all gases present pass through, but the mixture collected outside contains a larger proportion of the lightest gas than the original mixture, and by repeating we may make the separation more and more complete. This is called fractional diffusion, and is analogous to fractional distillation, wherein the completeness of the separation depends upon the number of times the process is repeated.

The Velocity of a Molecule. From the same formula, $\frac{1}{3} nmc^2 = pv$, we can calculate the probable velocity of a molecule. The density of mercury is 13.59; standard atmospheric pressure is 76 cm. of mercury, and therefore equal to $13.59 \times 76 = 1033+$ grams per cm^2. In order to convert this to units in the C.G.S. system, we must multiply it by the acceleration of gravity, or 981 dynes. Then p equals 1033 times 981. Let us carry out our calculation for the formula volume of hydrogen; that is, for 22 400 cm^3, under standard conditions. Then $v = 22\,400$.

We do not know the weight of one molecule of hydrogen, nor do we know the number of molecules of hydrogen in the formula volume. But the product of the mass of one molecule into the number of molecules must of course equal the weight of hydrogen. This volume under normal conditions weighs two grams; therefore $nm = 2$. Substituting in our equation, we have, $\frac{2}{3} c^2 = 1033 \times 981 \times 22\,400$. Solving this, we obtain the value 1845 meters for c. Therefore the average velocity of a hydrogen molecule under normal conditions of temperature and pressure is 1845 meters per second. There are about 1600 meters in a mile, and thus the average velocity of a hydrogen molecule at 0° is over one mile a second.

Evidently enough we may calculate the average velocity of a molecule of any other gas by the same method.

The Mean Free Path of a Molecule. Judging from these velocities, one would imagine that an odor liberated in one part of a room would fill the room with almost telegraphic rapidity, but we know that as a matter of fact an odor takes time to traverse the air. A gas does not diffuse instantly throughout a vessel containing another gas, and we think this is because its molecules can go but a short distance before colliding with other molecules which throw them back. Progress is then by a very intricate zigzag. The average distance traveled by a molecule before it strikes another is spoken of as the mean free path of that molecule, and it is usually designated by l.

There are three ways for calculating values for l. First, from the viscosity or internal friction of a gas; second, from its conductivity for heat; third, from the rate at which it diffuses. The results reached are nearly the same by all of these methods, so it is reasonable to suppose that we have obtained approximately the right magnitudes. Some of these values as calculated by O. E. Meyer for a temperature of 20° and 760 mm. pressure are as follows: H_2, 0.000 185 mm.;

CH_4, 0.000 085 mm.; CO, 0.000 098 mm.; CO_2, 0.000 068 mm.; NH_3, 0.000 074 mm.*

Size of a Molecule. There are several methods for estimating the size of molecules. Jeans† gives five: first, from the viscosity of gases; second, from the conductivity of gases for heat; third, from the diffusion coefficient; fourth, from the variations from Boyle's law; fifth, from the volume occupied by a gas as liquid or solid. He reaches the following values as the results of his calculations utilizing all these methods and ascribing double weight to the method from the viscosity of gases, as being the best:

DIAMETERS OF MOLECULES IN MILLIONTHS OF A MILLIMETER ($\mu\mu$).

H_2.....0.208	CO.....0.286	Air.....0.284
He 0.181	C_2H_4 ....0.381	NO 0.282
H_2O 0.339	N_2.....0.291	O_2 .....0.273
A 0.279	N_2O.....0.352	C_2H_3Cl...0.468
CO_2.....0.336		Cl_2.....0.411

The diameter of carbon dioxide molecules has been given as 0.29 millionths of a millimeter. These values are not the same, but are of the same order of magnitude, and that is all we pretend to have estimated by these methods.

Estimates by Other Methods. There are several other phenomena which enable us to estimate the probable size of molecules and atoms. Several of the most interesting we owe to Lord Kelvin.‡ Given a soap bubble of definite size, we must do work to increase its size. In the same manner, given a film of water of certain area, we must do work to increase this area. If matter were continuous, we might do an indefinite amount of work and increase the area indefinitely while at the same time the film would become indefinitely thin. If, on the other hand, the water is made up of individual molecules, we must imagine that when a certain area is reached, the film is only one molecule thick. Further extension will result in separation of the molecules and this separation may be carried so far that the molecules no longer hold themselves together as a film of water but fly off independently as gaseous molecules.

We may imagine that, substantially, we do this when we boil water.

* See "Die Kinetische Theorie der Gase," by O. E. Meyer (1895).

† J. H. Jeans, *Phil. Mag.*, 8, 692–699 (1904).

‡ See Sir William Thomson (Lord Kelvin), "Popular Lectures and Addresses," London (1889), Vol. I, p. 147.

We know the amount of heat required to convert water at its boiling point to steam at the same temperature, and we call it the heat of vaporization. We know the mechanical equivalent of heat, and so we know the amount of work which must be done to convert a definite quantity of water to steam. Let us imagine this amount of work applied to stretching out this amount of water into a thin film. We know how much work is required to stretch a film containing a definite quantity of water and of definite area until the area is increased to any given size. Therefore we can calculate the area which would be covered by a film if all the work represented by the heat of vaporization went to stretching it; and knowing the quantity we know also the thickness. This thickness must contain at least one molecule; it may contain more, but certainly cannot contain less. It is then an upper limit larger than which the diameter of the molecule cannot be. Lord Kelvin calculated this upper limit as about 10^{-8} centimeters. The diameter of a molecule of water is then about 1×10^{-8} centimeters, or 100 000 000 of them in a row and touching would measure one centimeter.

To get the number in a cubic centimeter, we must cube this and so obtain 10^{24} as the number of molecules of water probably present in one cubic centimeter of the liquid. Liquid water has a specific gravity about 1200 times that of gaseous water at 100° and 760 mm. Therefore this number must be divided by 1200 to obtain the number of molecules present in a cubic centimeter of gaseous water. In this way we obtain the value 8.3×10^{20}.

From the kinetic theory it has been estimated that there are 2.5×10^{19} molecules in a cubic centimeter of any gas under normal conditions. These two values are not the same, but still they are of the same order of magnitude.*

Siedentopf and Zsigmondy's Results. By the ultramicroscopic methods to be described in Chapter XIX, Siedentopf and Zsigmondy

* Another method suggested by Lord Kelvin is based upon electrical contacts; another upon diffraction phenomena, and the interference of light waves passing through two films; another upon the thickness of the deposit of a metal upon an electrode necessary to give the electromotive force characteristic of the deposited metal.

Faraday pounded out gold leaf until it was between four and eight millimicrons thick. These sheets were transparent and green. When heated slightly they lost all color, and yet, under the microscope, they appeared to be continuous, showing no holes. By depositing gold on glass, Faraday believed he obtained layers not more than one-tenth the above thickness. Of course these layers must be at least one molecule thick.

actually saw particles estimated as six-millionths of a millimeter in diameter. Such a particle would, according to the above calculation, have between 10 and 60 molecules in a row. If we assume the particle to be a cube, we must cube these values and then may say that the smallest particles ever distinguished must contain between one thousand and two hundred and sixteen thousand molecules. It is not at all likely that future developments of ultramicroscopic methods will enable us to see individual molecules, for it is easy to calculate that such a small particle would have to emit light of considerably greater intensity than the sun itself in order to be visible.

The best direct vision microscope is just able to distinguish a line one-tenth of a micron broad. Bacteria are in the neighborhood of half a micron in diameter by a few microns long, so the smallest bacterium must consist of many million molecules.

Brownian Movement. When we examine, under a microscope, a suspension or colloidal solution containing particles about 1 μ in diameter, they are seen to be in motion, oscillating through distances about equal to their own diameters. If the particles are smaller, the distances through which they oscillate are greater. When the diameters are about 4 μ, the motions are hardly perceptible. Using the ultramicroscopic methods by which smaller particles may be observed, it is seen that particles with diameters between 10 and 40 $\mu\mu$ travel on the average something like 20 μ in a straight line and then suddenly change their direction. They describe extraordinary zigzags with what, under the magnification, appears to be great velocity. In colloidal gold solutions, particles between 10 and 50 $\mu\mu$ in diameter have a velocity of about 100 μ per second. There is no gradual coming to rest; the motion is a perpetual motion, like that of the planets and stars. Particles suspended in liquids which were enclosed in granite countless years ago are still dodging about as they doubtless have been dodging for centuries. This interesting motion is named "Brownian movement" from Robert Brown (1773–1858), an English botanist who first observed it in 1827 with grains of pollen.

J. Perrin has made observations upon the Brownian movements of colloidal particles, and by ingenious methods has shown that the behavior of these particles is exactly what the kinetic theory indicates would be the behavior of molecules of that size.* This is indeed a great triumph, for it almost brings the assumptions of the

* "Brownian Movement and Molecular Reality," by J. Perrin, translated by F. Soddy, 93 pp. (1910).

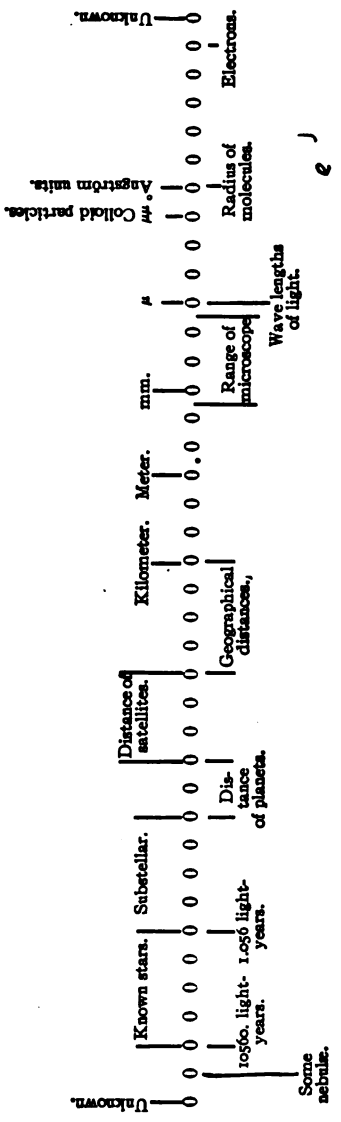
kinetic theory out of the region of hypothesis into the region of directly measurable laboratory fact. But "almost" stands for a wide gap because, according to our estimates, each one of these restless particles is large enough to contain many thousand molecules. In and by itself the argument is as if a bacteriologist should assert that a bacterium must consist of fifty thousand smaller bacteria, each moving rapidly, because he sees a bacterium move. It is a bit premature to speak of molecular "reality" upon this evidence alone.

Comparison of Our Measurements. The chart on the following page compares the largest and smallest dimensions which we have measured and estimated. It is based upon one published by G. J. Stoney* with a few additions and omissions. In the long decimal, reaching twenty-three places to the left and sixteen places to the right of the decimal point, a significant figure in place of a cipher is of the order of magnitude of the measurement indicated by words.

Extension of the Kinetic Theory. We obtain the kinetic theory by processes based on the behavior of gases, and this is such a useful mechanical model we apply it by analogy to liquids and solids, in short, to all substances. We should remember in doing this that our experimental bases are but few the moment we forsake the gaseous state. Nevertheless we think of liquids as multitudes of molecules moving about with different velocities, but so close together the mutual attractions keep them from flying apart. We think of solids as multitudes of molecules so close together their mutual attractions prevent their moving about among themselves, while probably permitting some degree of vibratory motion. The kinetic idea, the idea of the motion of the constituent molecules, has found its way into all processes and properties of substances when we think of those substances as above the absolute zero; that is, if they are supposed to contain any heat. In thought, at least, it has been carried further, until many are of the opinion that all we can observe is motion of some kind. Once more we arrive at the view that a universe of kinetic energy is what we study, what we know, and can observe, and that besides this there is a vast unknown about which we have only more or less plausible hypotheses.

Conduction of Heat by Gases. Another interesting deduction may be made from the kinetic theory of gases. We have assumed that heat corresponds to the average kinetic energy of molecules.

* "Survey of that Part of Nature's Operations which Man is Competent to Study," *Phil. Mag.*, 48, 457 (1899).


Unknown.
Known stars.
Substellar.
Distance of satellites.
Kilometer.
Meter.
mm.
μ
μμ
Colloid particles.
Unknown.
Some nebulæ.
1056 light-years.
1.056 light-years.
Distance of planets.
Geographical distances,
Range of microscope
Wave lengths of light.
Angström units.
Radius of molecules.
Electrons.

When heat is conducted by a gas, the average kinetic energy of the molecules must be increased. Either molecules with greater velocities pass through the interval conducting the heat, or else, by a succession of collisions, increase the velocities of the molecules at the other side.

The greater the velocity of the molecule, the faster such transference should take place. The lighter the molecules the greater their velocities; therefore, the lighter a gas specifically, the faster and better it should conduct heat. This deduction has been verified by experiments. Hydrogen conducts heat much better than any other known gas.

Specific Heat of Gases. We may define the specific heat of a gas as the number of calories required to raise one gram of the gas one degree centigrade. (Remember that the specific heat of a substance is different at different temperatures.)

Methods of Measuring the Specific Heat of Gases. Any instrument devised to measure the number of heat units given out by a process is called a calorimeter. Calorimeters are of a great variety of form, each adapted to some special purpose.

In measuring the specific heat of a gas it is convenient to cause a known volume of the gas to pass through a long spiral pipe immersed in water, the vessel containing the water being insulated from the surroundings as completely as possible. The temperature of the gas is determined as it goes in and as it comes out. The change in temperature of the water is also noted, and with a knowledge of the quantity of water and the heat capacity of the pipe, etc., we have the data necessary for determining the specific heat of the gas. Such experiments give us the specific heat under constant pressure, denoted by C_p.

Specific Heat of a Gas Varies. The specific heat of a gas under constant pressure is different from its specific heat under constant volume. When heat is added to a gas, not only is the gas warmed, but also it expands, and thus does work against any pressure there may be upon it. This is usually the atmospheric pressure. Then some of the heat added does not go to raising the temperature of the gas, but is converted into work.

We might cause the gas to expand while we added heat at such a rate that there would be no increase in temperature whatever; that is, the specific heat would appear to equal infinity. Or again, we might compress the gas, adding no heat, and there would be an

increase in temperature, and from such results we might argue that the specific heat was less than zero, a minus quantity. The specific heat of any gas is then anything between minus infinity and plus infinity, depending on conditions. We must, therefore, define our conditions carefully.

Specific Heat under Constant Volume. If the gas is in a rigid vessel such that no expansion can take place, all heat added goes to raise the temperature. Measurements made under these conditions give us what we call the specific heat under constant volume. This is denoted by C_v. C_p is greater than C_v by the heat equivalent of the work done by the gas expanding at constant pressure.

Determination of C_v.* J. Joly first made satisfactory direct determinations of C_v. He hung two equal copper spheres, about 6.7 cm. in diameter, from the pans of a balance, by wires, down into the interior of a chamber which could be filled with steam. He counterpoised the spheres, evacuated one and filled the other with a gas under pressure. In some experiments the pressures were as high as 22 atmospheres. Weighing, he determined the weight of the enclosed gas. In one experiment he had 4.2854 grams of air. He determined the temperature of his chamber and then let in steam. Suspended from the spheres were little catch basins in which the water condensing on them was caught. More water condensed on the sphere containing the gas, and determining the weight of this excess water it was a simple matter to calculate the specific heat of the contained gas.†

Molecular Heats. As usual, in chemistry, it is more profitable to compare equimolecular quantities than equal weights. The molecular heat of a gas, as the name implies, is the heat required to raise one molecular weight in grams 1°. It is then the specific heat C_v or C_p multiplied by the molecular weight M.

MC_p is, of course, greater than MC_v. Equimolecular weights occupy equal volumes, according to Avogadro's theory. When the

* See Preston, "Heat," p. 239. Also J. Joly, *Proceedings of the Royal Society*, 47, 218 (1889).

† Jamin & Richard, *Compt. Rend.*, 71, 336 (1870), determined C_p and C_v by sending a current through a platinum spiral immersed in the gas, with the vessel holding the gas first open to the atmosphere and then with it sealed. Heat evolved in the wire is C^2R, where C is the current and R the resistance, and by measuring the resistance and the current they determined the two different temperatures to which the gas was raised by a definite quantity of heat under the two conditions. The calculation followed readily.

pressure is constant, the increase in volume for one degree is the same for all gases. This is Gay-Lussac's law. Therefore, the work done against atmospheric pressure when a molecular weight of a gas is raised from zero degrees to one degree centigrade is the same for all gases. Therefore, $MC_p - MC_v$ is a constant.

The Value $MC_p - MC_v$. The molecular weight volume of any gas raised from 0° to 1° increases its volume $\frac{22\,400}{273}$ cm³ = 82 cm³ (about). Imagine the gas confined in a long tube of a cross section 1 cm². The normal atmospheric pressure is 1033 grams per cm², and so the gas expanding will raise 1033 grams 82 cm., and will then do $1033 \times 82 = 84\,680$ gram-cm. of work.

The mechanical equivalent of heat is, 1 cal. = 42 660 gram-cm. $\frac{84\,680}{42\,660} = 1.986$. Therefore, $MC_p - MC_v = 2$ calories (1.986 calories), no matter what the gas.

It is much easier to measure C_p than C_v, and we are justified by this reasoning in calculating the molecular heat under constant volume by simply subtracting two from the value of the molecular heat under constant pressure. Following is a short table of molecular heats. The fourth column in the table gives the ratio between the two specific heats, molecular weights of course canceling out.

	MC_p	MC_v	$\frac{C_p}{C_v}$
O_2	6.96	4.96	1.40
N_2	6.83	4.83	1.41
H_2	6.82	4.82	1.41
HCl	6.68	4.68	1.43
CO_2	9.55	7.55	1.26
H_2O	8.65	6.65	1.28*

* W. Ostwald, "Lehrbuch der allgemeinen Chemie," Vol. 1, p. 240.

The Ratio $\frac{C_p}{C_v}$. Clausius showed that if all energy went to increasing the rectilinear velocities of the molecules, $\frac{C_p}{C_v} = 1.66 +$.

This may be deduced from the kinetic theory of gases as follows: $pv = \frac{1}{3} mnc^2 = \frac{1}{3} Mu^2$ where $M = mn$ and u is substituted for c to avoid confusion.

Assume all energy given in increasing the temperature from 0° to 1° goes to increasing the rectilinear velocities while the volume is held constant. Let u_0 and u_1 equal the velocities of the molecules at 0° and at 1°.

Then $$\frac{Mu_1^2}{2} - \frac{Mu_0^2}{2} = MC_v, \text{ or } MC_v = \tfrac{1}{2} M (u_1^2 - u_0^2).$$

When the pressure is constant we require energy as above, plus that doing outside work. Outside work equals p times the increase in v,

or $$p(v_1 - v_0) = pv_1 - pv_0;\ pv_1 = \tfrac{1}{3} Mu_1^2, \text{ and } pv_0 = \tfrac{1}{3} Mu_0^2.$$

Then $$pv_1 - pv_0 = \tfrac{1}{3} Mu_1^2 - \tfrac{1}{3} Mu_0^2 = \tfrac{1}{3} M (u_1^2 - u_0^2);$$

so $$MC_p = \tfrac{1}{2} M (u_1^2 - u_0^2) + \tfrac{1}{3} M (u_1^2 - u_0^2) = \tfrac{5}{6} M (u_1^2 - u_0^2),$$

and $$\frac{C_p}{C_v} = \frac{\frac{5}{6}(u_1^2 - u_0^2)}{\frac{1}{2}(u_1^2 - u_0^2)} = \frac{5}{3} = 1.66+.$$

Experimental Determination of the Ratio. The ratio may be determined directly by the methods described, but it is difficult to determine C_v because a sufficiently rigid vessel has so large a heat capacity.

Kundt's Method. Another much used method is that of Kundt, whereby the ratio $\frac{C_p}{C_v}$ is derived from the velocity of sound in the gas.

Lycopodium is evenly distributed through a combustion tube about three feet in length, corked at each end and full of the gas. A glass rod projects through one cork. A high note is produced by rubbing this rod with a cloth covered with resin. We determine the number of vibrations a second corresponding to this note by the usual physical method, and then count the little piles of lycopodium which have formed at each node in the vibrating gas. From these determinations, the velocity of sound in the gas is readily calculated.

Newton showed that the velocity of sound should equal $\sqrt{\frac{p}{d}}$, where p is the pressure, and d the density, of the gas. Newton's formula does not hold* and Laplace found that $u = \sqrt{k \frac{p}{d}}$, where k = the ratio $\frac{C_p}{C_v}$ and u = the velocity of sound.

If we insert the value for u found by Kundt's method in Laplace's formula we may then calculate the value of k or $\frac{C_p}{C_v}$.

* See Preston's "Heat," p. 253.

Results. Almost all gases give values less than 1.66+. Mercury vapor, argon, and other rare gases of the atmosphere give the theoretical value, 1.66+. Other gases require more heat to raise them one degree than would appear necessary theoretically. Therefore something must be wrong with our fundamental assumptions. It is probably erroneous to assume that all the energy we give a gas when we heat it goes to increasing the rectilinear velocities of the molecules.

A simple hypothetical example may assist in understanding the reasoning. Suppose it requires five calories to raise a quantity of a gas 1° under constant pressure, and three calories to raise the same quantity 1° under constant volume, then $\frac{C_p}{C_v} = \frac{5}{3} = 1.66+$, the theoretical value, assuming that all the heat is converted to increased velocity of the molecules. Suppose now that all the heat does not go to increasing these velocities, but that some, say one calorie, is converted into something else. Then to raise the gas 1° under constant pressure we must give it 6 calories and to raise it 1° under constant volume we must give it 4 calories. Our ratio then becomes $\frac{6}{4}$ or 1.5. Thus we see that if any heat is converted into anything other than rectilinear motion the ratio will fall out less than 1.66+.

The ratio is less than 1.66+ for almost all gases and the question is, what becomes of the extra heat?

Explanation on Kinetic Grounds. It is reasonable to suppose molecules may have, besides motions in straight lines, motions of rotation about their axes, and again, the relative positions of atoms within the molecule may perhaps change; there may be vibrations within the molecule. Then part of the heat given may go to increase such motions. There is no difficulty in forming such a mental picture for a molecule containing two or more atoms.

Monatomic Gases. It is inferred, although the logic here is not particularly good, that if the molecule consists of one atom it cannot take up heat in the form of rotation about its axis. It is customary to conclude that when $\frac{C_p}{C_v} = 1.66+$, that is to say, when we have reason to believe that all heat goes to increasing the rectilinear velocity of the molecules, and that none is absorbed as motion of rotation, the gas is monatomic.

This is the reasoning upon which we base the theory that mercury, argon, helium, etc., are monatomic gases.

Nature of Heat. The facts lead us to conclude that heat consists (*a*) of rectilinear velocity of molecules, (*b*) of motion of rotation, or vibration, where the molecule is supposed to contain two or more atoms. But heat cannot be supposed to consist, even in part, of rotation or vibration of atoms or of events within atoms.

In so far as events within atoms is concerned we have independent corroborative evidence. The radiations from radioactive substances are supposed to result from the disintegration of atoms. This process is not hastened nor retarded by changes of temperature, and it surely would be if electron motion were a form of heat.

Exceptions to the Gas Laws. Gases are too compressible when near their points of condensation and not compressible enough under high pressure.

Andrews' Isotherms.* On a coördinate system, lay off pressures on the abscissa, and on the ordinate lay off values obtained by multiplying the pressure into the volume, temperature being held constant. In this way, if the behavior of the gas is exactly formulated by the gas laws, we obtain a horizontal line *AD*, in Fig. 14. Experimental results, however, give such curves as those shown, which are isotherms for carbon dioxide at the temperatures indicated on the figure. The product *pv* diminishes to a minimum and then rises as the pressure is increased. Some gases show less, others more, deviations from the horizontal. Isotherms for hydrogen and helium show no dip, but rise from the lowest pressures, except when the experiments are carried out at exceedingly low temperatures.

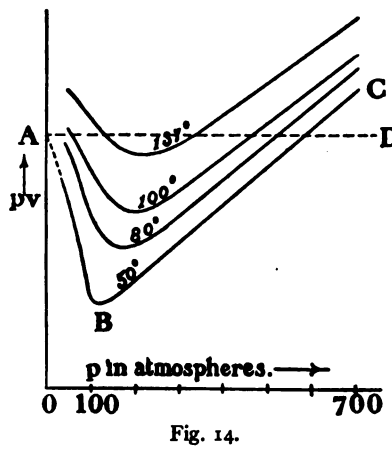


Fig. 14.

Van der Waals' Reasoning. We owe our plausible explanation for this behavior of gases to van der Waals.† His reasoning is as follows:

* Thomas Andrews (1813–1885), *Phil. Trans.* **159**, 575–589 (1869). See also Ostwald's "Klassiker der Exakten Wissenschaften," No. 132.

† J. D. van der Waals' first publication of the principles involved, "Dissertation," Leyden (1873), developed in "Die Kontinuität des gasförmigen und flüssigen Zustandes" (1881). Later edition with the same title, 1899.

The measured volume of a gas is v. The gas laws may be considered as applying only to the volume not occupied by the gas; *i.e.*, to the interstices between the molecules. Let b equal the volume to which the gas laws do not apply. For reasons upon which we shall not here enter, this is supposed to be about four times the volume occupied by the molecules themselves. Whatever it may actually represent, this is a constant value (or nearly constant value) characteristic for each gas, and different for different gases. The volume to which the gas laws apply is, then, $v - b$. If this correction be neglected, the values for the product pv will come out larger than they should.

Illustration. Imagine the measured volume to be 3, and the correction b to have the value 1. Then the volume to which the gas laws apply is 2. Doubling the pressure diminishes this to 1, and adding the constant, b, which has not been altered, we have as a final volume, 2. If we neglect to consider this correction, we should expect upon doubling the pressure to halve the whole and obtain the final volume 1.5.

When the pressure is low and the volume is large, b, being constant, is relatively small and may be neglected. That is, the gases conform to the law.

The Correction for Pressure. The molecules of a gas must be considered as having a certain attraction for each other. Van der Waals calculated that this attraction varies inversely as the square of the volume.

Van der Waals' Equation. Let a be a value expressing this attraction, constant (or nearly constant) for any one substance, and characteristic of it, but different for different substances. This attraction acts in a way to diminish the velocities with which the molecules are flying, and hence to diminish the pressure exerted by the gas on the containing wall. Therefore, the observed pressure should be corrected by adding the term $\frac{a}{v^2}$ to it. If p equals the measured pressure, then the pressure to which we may expect the gas laws to apply is $p + \frac{a}{v^2}$. Neglect of the pressure correction must result in values for the product pv which are too small. The gas equation then, in its corrected form, becomes $(v - b)\left(p + \frac{a}{v^2}\right) = RT$. This is called van der Waals' equation.

Effects of the Corrections. If the volume is not corrected, the product pv is too large. If the pressure is not corrected, the product pv is too small. When we have a large volume and a low pressure, b is negligible. v^2 is also large, and therefore $\frac{a}{v^2}$ is small and likewise negligible. That is, the gas and the gas laws should correspond. As the pressure is increased, the gas being not far from its point of condensation, the molecules are near each other, the mutual attractions are effective, and the pressure correction predominates. That is, the observed pressures are smaller than they should be and the gas is too compressible. This explains the downward inclination of the curve from A to B. When the volumes have become still smaller, b becomes larger compared to v, until finally this volume correction predominates, and the gas is not compressible enough. This explains the ascending of the isotherm from B to C. There is a point B where these two corrections just balance each other and for a short time the gas conforms exactly to the gas laws. This corresponds to a tangent drawn to the lowest point in the isotherm.

The equation opens up many more new and interesting questions than it answers. It contains three variables, p, v, and T, and three constants, a, b, and R. By determining experimentally three sets of corresponding values for p, v, and T and substitution, numerical values for the constants may be calculated. The equation containing these constants formulates the actual behavior of a gas much better than the uncorrected equation, but it is by no means perfect.*

The chief interest centers in the question as to what significance

* For the following numerical illustration of the effect of the correction see Baynes, *Nature*, **23**, 186 (1880). For unit volume of ethylene at 20° at a pressure of one atmosphere $a = 0.007\,86$ and $b = 0.0024$. Expressing pressures in atmospheres Baynes calculated values for pv and compared them with the pv values determined experimentally by Amagat and found:

	1000 pv			1000 pv	
p	Observed	Calculated	p	Observed	Calculated
31.58	914	895	133.26	520	520
45.80	781	782	176.01	643	642
72.86	416	387	233.58	807	805
84.16	399	392	282.21	941	940
94.53	413	413	329.14	1067	1067
110.47	454	456	398.71	1248	1254

we shall attach to the constants. In the first place we must realize that these values are not rigidly constant but depend in turn upon the values of the variables; *i.e.*, upon the conditions. Do not, on this account, think they should not be called constants. It was brought out in Chapter III that the gravitation constant itself is not constant except in one definite place.

Correcting the Molecular Volume. Let v_0 = volume in liters occupied by one molecular weight in grams of a gas under standard conditions, as determined by dividing the sum of the symbol weights in the formula by the weight of one liter. If Avogadro's theory was an accurate statement, v_0 would be 22.4 liters, the same for all gases. It has already been stated that the value 22.4 is only approximately constant, which of course carries with it the statement that Avogadro's theory is only an equally good approximation. The actual values of v_0 for a number of gases are given in the following table.

Now $\left(p + \frac{a}{v^2}\right)(v - b) = RT = \frac{p_0 v_0}{273} T$. At standard conditions, $T = 273$ and $p = 760$ mm., or one atmosphere, and for these conditions we may rewrite the above equation in the form

$$\left(1 + \frac{a}{v_0^2}\right)(v_0 - b) = [v_0],$$

wherein v_0 is the actual, experimentally determined value, and $[v_0]$ is a sort of idealized volume obtained with due consideration of van der Waals' corrections.* The table contains values for $[v_0]$. It may be seen at a glance that $[v_0]$ is more nearly constant than v_0.

	M	v_0	$[v_0]$
H_2	2.016	22.4452	22.4308
CO	28.00	22.3983	22.4084
O_2	32.00	22.3970	22.4140
CO_2	44.00	22.2635	22.4146
C_2H_2	26.016	22.2227	22.4109
HCl	36.458	22.2216	22.3983
SO_2	64.06	21.8890	22.4174

Clearly, van der Waals' equation leads to a more constant gas "constant" than the uncorrected equation.†

* D. Berthelot, *Zeitschr. f. Electrochem*, 10, 621–629 (1904).

† For additional values and further details and references see P. A. Guye, *Journal de Chim. Phys.*, 6, 769–807 (1907). Also, G. Baume, *ibid.*, 1–91.

The Constants a and b. The constants a and b may be determined from the coefficient of compressibility of a gas and also from the critical constants, as will be indicated later. The values obtained by the two methods are not the same. They are different at different temperatures and also different at the same temperature but different pressures.*

We must then conclude that the volume occupied by the molecules, and to which the gas laws do not apply, b, and also the attraction constant between the molecules, a, different for different substances but, in a sense to be likened to the gravitation constant in each substance, both vary with temperature, pressure, and volume. But they remain within the same order of magnitude and indicate a profound regularity of nature which we have not yet satisfactorily formulated.

* The following table gives some values of a and b for CO_2 at 40°, when volume is varied by varying pressure.

v	a	b
0.02385	0.01342	0.00545
0.01300	0.01240	0.00444
0.00768	0.01081	0.00325
0.00428	0.008138	0.00211
0.00250	0.007892	0.00169
0.00187	0.009245	0.00153

"Die Zustandsgleichung der Gase und Flüssigkeiten und die Kontinuitätstheorie," by J. P. Kuenen (1907), p. 76. This book is recommended to those desiring to pursue the subject in its manifold aspects.

CHAPTER XII

VAPOR DENSITIES*

In General. In Chapter IV we defined molecular weight as synonymous with formula weight, and this is the weight in grams of 22.4 liters of the substance as a gas under standard conditions of temperature and pressure. Therefore any method of determining the density of a gas is a method of determining its molecular weight. Also, by definition, the molecular weight of a gas is its density referred to oxygen set equal to 32 as a standard. In other words, for a vapor density determination, or a molecular weight determination, which is the same thing, it is necessary to determine experimentally the four values, weight, volume, pressure, and temperature, and any method whatever which gives us these values serves the purpose. From these experimental results we calculate the weight in grams of 22.4 liters of the substance as a gas under standard conditions, or institute the comparison between the unknown and the weight of an equal volume of oxygen under the same conditions.

First Method. The first method is, in principle, very simple, and corresponds to the usual specific gravity determinations. We may weigh a flask empty, then full of the standard, that is, oxygen, then full of the gas whose molecular weight is sought. We must at the same time note the temperature and barometric pressure, unless they are the same throughout the experiments, and these results are sufficient for the calculation.

This method is difficult in practice for the following reasons: (*a*)

* It is not intended, in this book, to give full laboratory directions. For these the student should consult such excellent manuals as "Practical Physical Chemistry," by Alexander Findlay, 281 pp. (1906); "Laboratory Exercises in Physical Chemistry," by F. H. Getman, 241 pp. (1904); "Practical Methods for Determining Molecular Weights," by H. Biltz, translated by Jones and King, 235 pp. (1899). The standard work on the subject is: "Hand- und Hülfsbuch zur Ansführung Physiko-Chemischer Messungen," Ostwald-Luther-Drucker, third edition, 573 pp. (1910).

However, in view of the fact that vapor density determinations are so intimately connected with the establishment of the chemical unit quantities which enter into all our reasoning, it seems desirable to treat of them in some detail.

Rather large flasks must be used to hold conveniently weighable quantities of a gas. (*b*) It is hard to get a perfect vacuum within the flask. (*c*) The atmospheric pressure on the sides reduces the size of the flask, and therefore the weight of air displaced by the evacuated flask is less than by the full flask. (*d*) The weights of such volumes of gases as are used are small, and the weights of the flasks are large. This requires sensitive balances, capable nevertheless of carrying rather large loads. (*e*) Films of moisture on the exterior of glass flasks are hard to remove completely, and yet these materially alter the weights.

This method is obviously limited to substances which are gaseous under ordinary conditions of temperature and pressure. It has therefore but few applications.

The Vapor Density Methods. There are four methods in general use for determining the vapor density of gases, each dependent on a somewhat different principle. In historical order they are the Dumas, the Hofmann, the Victor Meyer, and the Bleier and Kohn, also known as Lumsden's method. They are applicable to substances which are solid or liquid at ordinary temperatures, but which vaporize without decomposition at somewhat higher temperatures. They are limited to these substances.

Dumas Method. In the Dumas method, we determine the weight of the substance which, as a vapor, occupies a known volume under known conditions of temperature and pressure.

A bulb of a capacity from 100 to 250 cm^3, or even larger, and furnished with a narrow tube, perhaps eight or ten cm. long, is cleaned and dried and the stem is drawn out to a capillary. The whole is weighed. This gives the first experimental value. Call it "weight *a*." Weight *a* is the weight of the bulb, plus the weight of the air contained within the bulb, minus the weight of the air displaced.

We warm the bulb gently, dip the capillary in a little of the liquid whose vapor density we wish to determine, and allow it to cool. The air within contracting, four or five cubic centimeters of the liquid are drawn into the bulb. The bulb is then wholly immersed in a bath, only the stem projecting out. The temperature of this bath is then raised to thirty or forty degrees above the boiling point of the liquid within. The liquid first boils and displaces all of the air, and then continues to expand. Figure 15 illustrates a bulb in the bath.

At this high temperature, and when the outflow of gas is slow and

regular, the capillary is sealed by means of a blow pipe. The temperature must constantly rise until the sealing has been accomplished. If it should fall, even for a short time, some air would be drawn into the bulb, and this would produce a notable error in the results. The sealing temperature must be thirty or forty degrees above the boiling point of the substance, because the gas laws do not apply when gases are near their points of condensation, and our calculations are based on the assumption that they do apply. Let us denote the temperature of the bath when the bulb is sealed with t_2. The barometric pressure is read immediately, and we shall denote this with p_2. The sealed bulb is removed from the bath, dried, cooled and weighed. This weight we shall call "weight *b*." It is the weight of the bulb, plus the weight of the vapor within, minus the weight of the air displaced. The fact that the vapor has condensed of course makes no difference. The quantity of substance within the bulb is the amount which was necessary to exactly fill the bulb at the temperature of sealing, and its weight is not altered by the cooling or condensation. Let t_1 and p_1 represent the temperature and barometric pressure when "weight *b*" is determined.

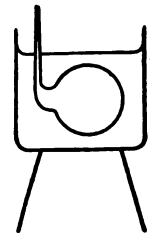


Fig. 15.

We then break the capillary under recently boiled water, and owing to the diminished pressure the water practically fills the bulb. The completeness of this filling is a check on previous work. If air remained in the bulb, it will not fill with water. There is always a small bubble of air, but this may be neglected for ordinary work. It is essential that the water should have been recently boiled, because, if it contains dissolved air, under the diminished pressure this comes out and makes too large a bubble.

The temperature of the water must be noted. Call this t_3. We now weigh the bulb full of water. Call this "weight *c*." Weight *c* is the weight of the bulb, plus the weight of the water, minus the weight of the air displaced. This concludes the experimental portion of the work and we may now proceed to the calculation.

Calculation. The following method is not exact, but it is sufficiently accurate for ordinary laboratory practice. We may consider *a* as the weight of the bulb, because the weight of the contained air is very nearly the weight of the displaced air. It is different only by the weight of the air displaced by the glass from which the bulb is made, a quantity small enough to neglect in most cases.

$c - a$ is then the weight of the water which fills the bulb. The weight of air displaced is negligible in comparison with the weight of the water. The error brought into the calculation here is about one-tenth of one per cent only.

By reference to tables* we find the volume occupied by one gram of water at the temperature t_3. Say this is e cm³. Then the volume of the contents is $e\,(c - a)$.

$b - a$ is equal to the weight of the vapor minus the weight of an equal volume of air; and of course this latter quantity cannot be neglected, as it frequently amounts to as much as the weight of the vapor itself.

One cm³ of air at zero degrees and 760 millimeters weighs 0.001 293 gram. At t_1 and p_1 one cm³ becomes, according to the gas laws, $\frac{760}{p_1}(1 + 0.003\,67\,t_1)$ cm³. Then, $\frac{e\,(c-a)\,0.001\,293}{\frac{760}{p_1}(1+0.003\,67\,t_1)}$ = weight of the volume of air which is equal to the volume of the vapor, very nearly. Call this A. Then $b - a + A$ = weight of vapor = x. Then $e\,(c - a)$ cm³ of the vapor at t_2 and p_2 weighs x grams.

We may calculate the weight of an equal volume of oxygen under the same conditions of temperature and pressure. One cm³ of oxygen at 0° and 760 mm. weighs 0.001 429 gram. One cm³ will become, according to the gas laws, $\frac{760}{p_2}(1 + 0.003\,67\,t_2)$ cm³ at t_2 and p_2. Then $\frac{e\,(c-a)\,0.001\,429}{\frac{760}{p_2}(1+0.003\,67\,t_2)}$ = weight of an equal volume of oxygen at the same temperature and pressure. Call this y. Then $x : y = M : 32$, or $M = \frac{32x}{y}$, where M = the density or molecular weight sought.

Corrections. For accurate work other corrections must be applied, for instance: *first*, a correction for the air displaced by the weights; *second*, glass expands and the bulb holds more at a high temperature than at a low temperature, therefore, we should correct for the cubical expansion of glass; *third*, when the vapor has condensed, a partial vacuum is produced, and the atmospheric pres-

* The standard reference work for numerical constants, and tables in great variety, is "Physikalisch-Chemische Tabellen," Landolt-Börnstein-Meyerhoffer, third edition, 861 pp. (1905).

Van Nostrand's "Chemical Annual," edited by J. C. Olsen, 580 pp., second issue (1909), contains the most used tables.

sure reduces the size of the bulb, which then displaces too little air; *fourth*, the method is subject to a characteristic source of error. If a substance contains an impurity of high boiling point, the substance will boil off and the bulb may contain mainly the impurity at the time of sealing. On the other hand, if the impurity boils at a lower temperature than the substance, it is driven off, and the determination is made upon purer material than the original sample.

Discussion. The Dumas method is useful over a wide range of temperatures, as the bulb may be made of porcelain instead of glass, and baths of molten metals may be used. It requires a longer time for the experimental part and more calculation than the other three methods, but it gives remarkably good results in the laboratory, even in the hands of beginners.

Hofmann Method. In the Hofmann method we vaporize a known weight of a substance at a known temperature, and measure the volume which it occupies at this temperature.

A graduated tube containing at least 100 cm^3 is filled completely with clean mercury. Air bubbles are swept out with a feather, or by flowing the mercury to and fro. A minute bottle with a glass stopper is weighed empty, filled with the substance, weighed again, and the difference in weights is the weight of substance taken. Or a small, thin-walled bulb with a capillary stem is blown, weighed empty, filled with the liquid, sealed, and weighed again. The difference in weights gives the weight of the substance. This small bottle or bulb containing the weighed amount of the substance is inserted in the graduated tube while the latter is held in a slanting position. The tube is then brought to a vertical position over a trough of mercury. If the bottle or bulb is inserted while the tube is in a vertical position the bottle may open, or the bulb may burst, before it has reached the surface of the mercury. The force of the explosion is sometimes sufficient to drive mercury to the top of the tube and break it.

When the tube is brought to a vertical position the mercury drops. This is not an indication of leakage or the presence of air. There is a Torricellian vacuum at the top, and of course mercury will not stand higher than the barometric height.

A mantle surrounds the tube, and vapor from some substance boiling in a nearby flask is led into this mantle. The apparatus is shown in Fig. 16. When the temperature has become constant, and all the substance has vaporized, the volume of the vapor is read. The height of the mercury column is read also by means of a cathe-

tometer. A pendulum cathetometer with wires on two arms, so arranged that one wire may be on one side, the other wire on the other side of the mantle and tube, is a convenient instrument to use for this purpose. The wires of the cathetometer serve to keep the eye at the right level in all the readings.

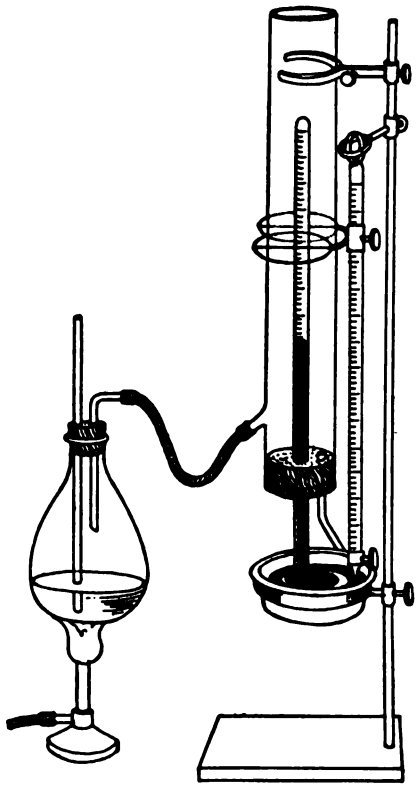


Fig. 16.

The barometric pressure is noted at once; the boiling point of the substance used for heating gives us the temperature (t_1) of the vapor in the tube surrounded by it, and the experiment is finished.

Calculation. Let x equal the weight of the substance, v the volume of vapor at t_1 and p_1, p the reading of the barometer, p_c the barometric reading corrected to zero degrees,* H the height of the mercury column from the surface in contact with the vapor to the surface in the trough, H_c the height of this mercury column corrected to zero degrees.

We may consider the mercury column as consisting of two parts, the length within the jacket, and presumably close to the temperature t_1, and the length without the jacket down to the trough. The mercury in the trough is at a decidedly lower temperature. The column conducts heat, and we may consider that this second section has a temperature approximately the arithmetical mean of the temperature in the trough and t_1. q = vapor pressure of mercury at t_1.† Then $p_c - H_c - q = p_1$.

* The mercury in a barometer at room temperature is specifically lighter than it would be at 0°. Therefore the actual reading is higher than it would be at 0°. Tables for this correction are contained in L.-B.-M., *loc. cit.*

† See tables, L.-B.-M., *loc. cit.*

q = 0.27 mm. at 100° and 8.53 mm. at 180°.

Now calculate the weight of an equal volume of oxygen at t_1 and p_1. Call this y. Then $x : y = M : 32$ and $M = \frac{32x}{y}$, where M is the vapor density or molecular weight sought.

Discussion. The Hofmann method is accurate and easy, and gives good results in the hands of beginners. Its range is small, as we must use glass and mercury, and mercury boils at 357° and glass softens not far above this temperature.

The diminished pressure has the same effect, so far as the application of the gas laws is concerned, as a higher temperature, and so it is not necessary that the vapor should be thirty to forty degrees above the boiling point of the substance. In fact, the method may be so adapted as to give useful results at temperatures even below those at which the substances boil under atmospheric pressure.

Victor Meyer Method. In the Victor Meyer method, we determine, by the air displaced, the volume a weighed amount of substance would have occupied as a vapor at the temperature of the room.

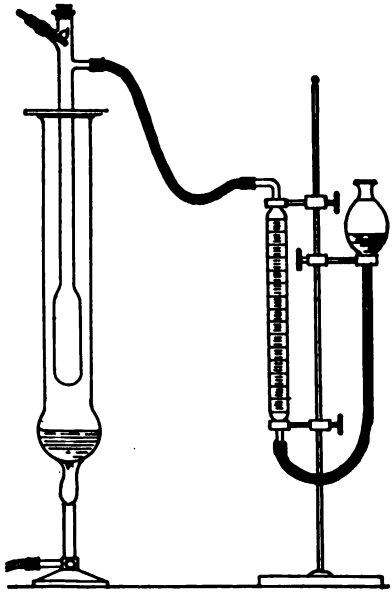


Fig. 17.

A small quantity of the substance is weighed out in a bottle or bulb as for the Hofmann method. The apparatus consists of an inner vessel, a tube a little less than one cm. in diameter, and perhaps 75 cm. long, enlarged at the bottom. The capacity of the enlargement is from 100 to 250 cm^3. This inner vessel is suspended in an outer mantle, wherein some substance is boiled to produce the necessary constant high temperature.

The little bulb containing the weighed amount of substance is inserted in the upper part of the inner vessel, and is prevented from falling by a glass rod which projects through a side tube. The joint between this glass rod and the side tube is made with flexible rubber tubing, gas-tight, but in such a way that we may pull out the rod and

permit the bulb to drop when we wish. Another side arm from the inner tube leads to a burette full of water or mercury furnished with a leveling bulb. The apparatus is shown in Fig. 17.

The liquid in the outer mantle is heated until it boils. The upper end of the inner vessel is closed and the level of the liquid in the burette is noted. If the temperature in the inner vessel has become constant, there will be no change in the level of the liquid in the burette.

When we are reasonably sure that the temperature has become constant and will remain constant for two or three minutes, we pull out the side arm and permit the substance to drop to the bottom. The impact and increased temperature breaks the bulb or drives the stopper out of the bottle, and the substance vaporizes at the bottom of the inner vessel. The vapor acts like a piston, forcing out or displacing the air, which is driven through the side arm and is collected in the burette. We alter the position of the leveling bulb and measure the increase in volume of air in the burette. The vaporized substance remains in the hot chamber, and what we measure is the volume of air displaced. This volume is the volume which the substance would have occupied if we could have had it as a gas at room temperature and the prevailing pressure. We need not know the temperature of the inner vessel if only we are sure that it is thirty or forty degrees above the boiling point of the substance we are investigating, and if we are sure it is constant throughout the experiment. We must be careful not to use too much substance or the vapor will fill the inner vessel so completely that it may rise to a cooler region and partly condense. This would of course vitiate our results.

It is well to place a layer of previously ignited sand, or of mercury, or of glass beads, or glass wool at the bottom of the inner vessel to protect it from the impact of the falling bulb or bottle.

If we use water instead of mercury in our burette, it should be saturated with air before the experiment is begun. The temperature of the water or mercury and the air in the burette is that shown by a thermometer hanging by its side. We read the barometer and the experiment is finished.

Calculation. Let x equal the weight of the substance, t_1 the temperature of the water, v the volume in cm^3 which we measured directly from the graduation on the burette, p_1 the pressure of the substance as a gas within the burette. This is equal to the barometric pressure less the vapor pressure of water at the temperature t_1.

We look up in tables this vapor pressure of water at t_1. Let it equal q. Then $p_1 = p - q$. If mercury is used this correction is not necessary. Calculate the weight of v cm³ of oxygen at t_1 and p_1. Let this equal y. Then $x : y = M : 32$ and $M = \frac{32x}{y}$, where M = the vapor density or molecular weight sought.

If we have many determinations to make, we can construct our apparatus with a large inner vessel and make a series of experiments in rapid succession; but in general we must not work slowly, because diffusion proceeds constantly, and, given time enough, the vapor will rise out of the hotter portion of the inner vessel to cooler regions and condense.

Discussion. This method has a wide temperature range. For instance, vaporizing vessels have been made of platinum and inserted directly in an electric furnace. It is the most used of all the vapor density methods.

Bleier and Kohn or Lumsden Method. In the fourth method we measure the change in pressure due to the vaporization of a known weight of substance while the volume and temperature are held constant. Apparatus utilizing this principle to determine molecular weights was devised by G. Dyson,* by Bott and Macnair,† by T. W. Richards,‡ by Bleier and Kohn,§ and by J. S. Lumsden.‖ Most generally used are the arrangements described in the last two articles, hence the method is commonly called Bleier and Kohn's or Lumsden's. Following is a description of Bleier and Kohn's apparatus.

Suppose we have a vessel which contains 22 400 cm³ and in it one molecular weight in grams of any gas at 0°. The pressure will be 760 mm. Suppose we have half a molecular weight in grams present; then the pressure will be only $\frac{1}{2}$ of 760. Or, the pressure observed is the same fraction of 760 mm. as the amount of gas present is of a molecular weight in grams.

Imagine that the vessel is empty and that we put into it fifty grams of a gas of unknown molecular weight. We measure the

* *Chem. News*, **55**, 88 (1887).

† *Berichte d. chem. Ges.*, **20**, 916–922 (1887).

‡ *Chem. News*, **59**, 87 (1889).

§ *Monatshefte f. Chem.*, **20**, 505–538 and 909–925 (1899).

A review of their articles may be found in *Jour. Chem. Soc.* (London) **76**, 643, (1899).

‖ *Jour. Chem. Soc.* (London) **83**, 342–349 (1903).

pressure and find it to be 190 mm. Then $\frac{190}{760}$ is the fraction of a molecular weight present. Let M = the molecular weight. Then $M\frac{190}{760} = 50$, or $M = 200$.

Suppose the vessel is not entirely empty, but contains enough of some indifferent gas to exert a pressure of 380 mm. $\frac{380}{760} = \frac{1}{2}$. One-half a molecular weight is present. Let us add one-fourth of a molecular weight in grams of some other gas. There will then be present three-fourths of a molecular weight, and the pressure will be $\frac{3}{4}$ of 760, or 570 mm. $570 - 380 = 190$ mm. That is, we obtain the same increase in pressure as if the gas had been put in the empty vessel. Then the increase in pressure caused by adding a quantity of a gas is the same fraction of 760 as the weight of the added gas is of a molecular weight, whether something else be present or not.

Let Δp equal the observed increase in pressure and g, the grams of substance. Then $\frac{\Delta p}{760} = \frac{g}{M}$.

But we are not confined to a vessel of this particular size. We might use one only half as large. Then a molecular weight in grams present would exert double the normal pressure, or 2×760, *i.e.*, 1520 mm. and our formula would become; $M = \frac{g}{\Delta p} 1520$.

For any vessel, we can calculate the pressure which would be exerted by a molecular weight in grams of a gas within it. This pressure is of course a constant as long as the volume and temperature remain constant. Let us call it the constant for the vessel and denote it by c. Our formula may now be written in its final form; $M = \frac{g}{\Delta p} c$.

For the sake of simplicity we reasoned on the assumption that the temperature was zero. But what has been said will hold just as well for any other temperature as for zero. It is only necessary that the temperature be held constant. For example, suppose with our original vessel and one molecular weight of any gas in it, we raise the temperature to 100°. From the third gas law we know, that when v is held constant, the pressure increases as the absolute temperature, or $p : p_1 = T : T_1$, then $760 : p_1 = 273 : 373$, from which $p_1 = 1038+$. Thus c, the increase in pressure produced by the addition of a molecular weight in grams of any gas, is not 760 but 1038+ under these other conditions. For any vessel at any temperature we may calculate a constant, c, and the formula will hold as given.

Description of Apparatus. The apparatus is a modification of Victor Meyer's, with the substitution of an adjustable manometer tube for the measuring burette and leveling bulb, as shown in Fig. 18. In carrying out an experiment we first weigh our substance in a small bottle or bulb, as for the Hofmann or Victor Meyer method. We reduce the pressure in the apparatus by means of a water pump and then close the stop cock, *C*, leading to the pump. By means of the leveling bulb we adjust the mercury meniscus at *A*. We read the position of the meniscus at *B*. After the liquid in the mantle has boiled long enough to bring the inner vessel to a constant temperature, we permit the bulb containing the weighed amount of substance to drop. It breaks and the substance vaporizes, and the mercury in the manometer falls from *A*. With the leveling bulb we bring it back to *A* exactly. Thus the volume is the same as at first. Of course, the other meniscus of the manometer is higher, at *D*. Then the distance from *B* to *D* is the increase in pressure produced by the vaporization of the known weight of substance. We insert this value in the formula $M = \frac{g}{\Delta p} c$ and calculate M very quickly if we know c.

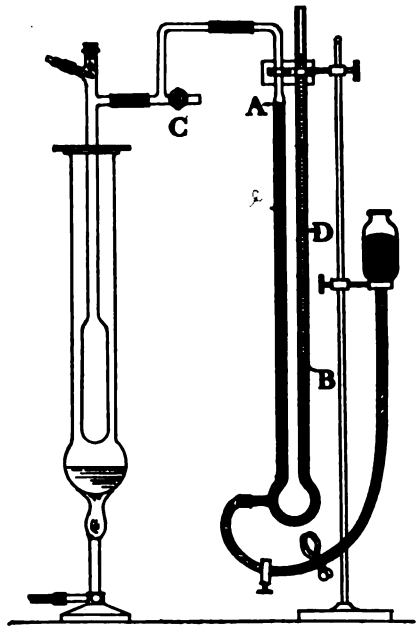


Fig. 18.

Determination of *c*. We may calculate the value of c in the manner already indicated if we know the capacity of the apparatus, but usually it is quicker and more convenient to determine it experimentally by carrying through an experiment with a substance of known molecular weight. By substitution in the formula, we may solve for c, and the value thus determined is the constant for that particular apparatus and temperature.

Of course with one and the same apparatus the values for c are different for different temperatures. They may be calculated from any one known value for c, but usually it is safer, as well as more convenient, to run through a preliminary experiment.

Discussion. The method is reasonably accurate. It is easily carried out, and the calculation is simple. The gas laws apply at low pressures as at high temperatures and so, exhausting the apparatus rather far, successful determinations have been made with it on substances as much as 90° below their boiling points. The method has as wide a range as the Victor Meyer method, for we may have the inner vessel at any temperature whatever, so long as that temperature is constant during the experiment.

There is little likelihood of unobserved error, for any leakage or inconstancy of temperature is at once noted by motion of the meniscus at A. If diffusion occurs and some substance gets to cooler parts and condenses, the resulting diminution in pressure shows itself in the same way. Error from this cause need not be feared if the vaporized substance fills not more than two-thirds of the heated part of the enclosed volume. The volume occupied by the vaporized substance is easily calculated from the measured increase in pressure. For instance, if the vaporized substance occupies two-thirds of the volume, the final pressure is three times the original pressure.

A source of error is inherent in this method. When the substance vaporizes it forces hot air to a cooler portion of the apparatus where it contracts. Thus the observed increase in pressure is always a little less than it should be. If about the same volume of vapor is produced when a molecular weight determination is being made as was produced when the constant of the apparatus was being determined, this error is negligible. An apparatus devised by Menzies for another purpose may be employed here in such a way as to eliminate this error. It is described and illustrated in Chapter XXIII, and its application in this connection is there explained.

Abnormal Vapor Densities. The density of ammonium chloride as a gas, to agree with the formula NH_4Cl, should be 53.5 when oxygen is 32; but it is less than this, and the higher the temperature, the lower the vapor density, to a minimum of 26.75. Henri Ste. Claire Deville suggested, in 1857, that the substance dissociates, one molecule of NH_4Cl giving one molecule of NH_3 and one molecule of HCl, thus doubling the number of molecules present. According to

Avogadro's theory, this doubling of the molecules should double the volume, and halve the density.

Pebal proved experimentally in 1862 that this dissociation actually occurs. He vaporized ammonium chloride in a tube of large diameter, at one side of a porous partition, which divided the tube into two chambers. At first he used unglazed porcelain, but later, to meet certain objections which were raised, he made this membrane of ammonium chloride itself. Ammonia, having a less vapor density than hydrogen chloride, diffuses through fine openings more rapidly, and in this way he separated the two gases, showing that the gas which came through the membrane had an alkaline reaction while the gas which remained behind showed an acid reaction with litmus paper.

Phosphorus Pentachloride. Phosphorus pentachloride as a vapor is colorless, but it dissociates according to the reaction, $PCl_5 = PCl_3 + Cl_2$. When the temperature is raised the vapor grows greener due to the presence of more chlorine, and we may follow the dissociation of the gas qualitatively by the color change.

Nitrogen Tetroxide. Nitrogen tetroxide, N_2O_4, is itself colorless, but it dissociates according to the reaction, $N_2O_4 = 2\ NO_2$. Nitrogen dioxide is a reddish brown. In this case also we can follow the progress of the dissociation qualitatively, for the mixture grows darker brown as the temperature becomes higher. At 500° the gas becomes colorless again, due to a second dissociation, according to the reaction, $2\ NO_2 = 2\ NO + O_2$. Both of these products are colorless.

Ammonium Carbamate. Such dissociation is not limited to a splitting into two parts. Ammonium carbamate, $CO(NH_2)(ONH_4)$, dissociates into $2\ NH_3 + CO_2$, one molecule giving three, and the vapor density of the substance diminishes to one-third of the calculated value.

Sulphur. Sulphur near its boiling point has a vapor density nearly corresponding to the molecular formula S_6. At 800° its vapor density corresponds to the formula S_2. It is almost universally stated that there is a molecule S_6 which splits to $3\ S_2$. In solution, by other methods, we get the molecular formula S_8.*

Comment. S_8 is not very different in its chemical properties from S_2. By analogy we might expect more, because, where it suits our

* G. Preuner and W. Schupp, *Zeitschr. f. phys. Chem.*, **68**, 129–156 (1909), have demonstrated very ingeniously that we probably have S_8, S_6, and S_2, and these only, between 300° and 850° if the pressure is above 30 mm.

convenience to do so, we ascribe even such marked differences as are observed between allotropic forms to no greater difference in the molecule. Here, on the other hand, we have a noteworthy difference in the molecule and relatively little in chemical properties. It is worth while to call attention to this usage, as it emphasizes the provisional nature of our theories. The plain fact is that the behavior of sulphur vapor does not anywhere near correspond with the formulation of the gas laws, and the most plausible hypothesis which has occurred to us as yet to account for these facts is gaseous dissociation.

Iodine. Up to 500°, iodine has a vapor density corresponding to the formula I_2. At 1500° and under diminished pressure, its vapor density corresponds to the formula I. The behavior of bromine and chlorine is similar.

Mercury. With mercury we have no such variation. The vapor density corresponds to the formula Hg from the lowest to the highest temperatures at which it has been measured.

Acetic Acid. Acetic acid shows the reverse phenomenon. Just above its boiling point its vapor density is greater than the value corresponding to the formula CH_3COOH, and we assume that it contains double molecules. We say that it associates or polymerizes.

Calculation of Degree of Dissociation. Let n equal the number of molecules obtained by the dissociation of one molecule. Let δ equal the vapor density in case there is no dissociation. Let Δ equal the vapor density observed. Let α equal the fraction of the whole which is dissociated.

For the sake of clearness, imagine that we start with 100 molecules. Then $100\,\alpha$ is the number dissociated, and these will give us by their dissociation $100\,\alpha n$ molecules. Then $100\,(1-\alpha)$ is the number left undissociated. Therefore the total number of molecules after partial dissociation has occurred equals $100\,\alpha n + 100\,(1-\alpha)$.

The greater the number of molecules the greater the volume, and the less the vapor density, according to Avogadro's theory. There is then an inverse proportionality between the vapor densities and the number of molecules. We may therefore write

$$100 : 100\,\alpha n + 100\,(1-\alpha) = \Delta : \delta.$$

Solving this, we obtain the expression $\alpha = \dfrac{\delta - \Delta}{(n-1)\Delta}$.

Some Data upon Degrees of Dissociation. Diminution of pressure acts like increase of temperature in increasing dissociation.

At high temperatures and low pressures, water dissociates in a measure to hydrogen and oxygen, and carbon dioxide to carbon monoxide and oxygen. The following tables give the percentage dissociated of these two substances at four different pressures and temperatures. The temperatures are on the absolute scale.*

Water.				
Temperature.	$P = 10$ atmospheres.	$P = 1$ atmosphere.	$P = 0.1$ atmosphere.	$P = 0.01$ atmosphere.
1000	0.0000139	0.00003	0.0000646	0.000139
1500	0.0103	0.0221	0.0476	0.103
2000	0.273	0.588	1.26	2.70
2500	1.98	3.98	8.16	16.6
Carbon dioxide.				
1000	0.00000731	0.0000158	0.000034	0.0000731
1500	0.0188	0.0406	0.0872	0.188
2000	0.818	1.77	3.73	7.88
2500	7.08	15.8	30.7	53.

Burning carbon to carbon monoxide gives but one-third as much heat as is obtained when it is burned to carbon dioxide. By reference to the tables we may estimate that under the conditions obtaining in a blast furnace there must be some loss due to dissociation, but that it cannot be serious.

It was thought that carbon could be burned more completely if blast furnaces were made much larger, and that this would result in an economy of fuel. It is evident that the completeness with which carbon is burned is not a function of the size of the furnace. This is an illustration of the value of theoretical considerations for practical problems. Anyone with a fair working knowledge of the theories of the science could have foretold that the object would not be gained by such increase in size. The enormous blast furnaces which were erected would have been costly and wasteful experiments if they had not produced economies in other ways.

Dissociation and Lighting. In the light giving zone of an illuminating gas flame the pressure of the CO_2 must be small and the

* These tables are taken from Nernst, "Theoretische Chemie," sixth edition (1909), p. 681.

temperature may be nearly 2000°; consequently some little heat must be lost by dissociation. The radiation is proportional to the fourth or fifth power of the temperature, so the net loss in lighting efficiency due to dissociation is not insignificant.

Dissociation and Explosives. In the case of explosions any dissociation would be advantageous but precisely here the pressures are so high the dissociation is negligible. The subject is one of importance in view of the increasing numbers of internal combustion engines.

Dissociation is Frequent. The phenomenon of gaseous dissociation is more frequent than was at first supposed. Probably everything is dissociated when hot enough and when the pressure is low enough, even the elements into single atoms and the atoms probably into simpler complexes of electrons.

Attempts to observe experimentally a dissociation of the molecules of nitrogen and oxygen have been conducted at temperatures estimated to be nearly 1700° at a pressure of 760 mm., but they gave negative results.

Conduction of Heat by Dissociated Gases. We have, in the experimental study of the conduction of heat by partially dissociated gases, a further argument in favor of the kinetic theory. Heat is conducted by a gas as the average velocity of the molecules. In all the instances cited, dissociation takes place with the absorption of heat and when the reverse reaction, association, takes place, heat is evolved.

Imagine a gas partly dissociated. An undissociated molecule in the hotter portion of the containing tube dissociates, thus taking up heat. It arrives at a cooler zone and there associates, thus giving up this heat. In other words, the conduction of heat should be more rapid when a gas is partially dissociated than when it is either not dissociated at all, or is completely dissociated.

It has been found experimentally that nitrogen dioxide in a partially dissociated condition conducts heat almost three times as well as when it is completely dissociated.

CHAPTER XIII

LIQUIDS

We define a liquid as a substance which has a definite volume, but no definite shape. This statement establishes the main difference between a liquid and a gas on the one hand, and a liquid and a solid on the other.

Kinetic Theory. We apply an analogy drawn from our study of gases and say that we believe liquids consist of molecules moving in straight lines and also about their axes. We assume that the molecules of a liquid move amongst themselves with comparative ease and so account for the fact that the liquid fills completely the bottom of any containing vessel. We also assume that the molecules of a liquid are close enough together to exert a mutual attraction in excess of the energy of the motion in straight lines. This, we suppose, restrains them from flying apart and filling completely any containing space, as does a gas. This attraction is the force which we denote by a in van der Waals' equation. The study of liquids furnishes no such regularities nor great generalizations as the gas laws.

Density. By density, sometimes called specific mass, we mean the mass, expressed in grams, contained in unit volume, (one cm^3). By definition the density of water at 4° is one, and we may neglect the slight error made in the original determinations of our units. (1 cm^3 water at 0° weighs 0.999 97+ grams.) Specific gravity is the ratio between two weights contained in equal volumes, and if water at 4° be taken as the standard of comparison it is the same as density.

Determination of Density. The hydrometer, also called areometer, consists of a weighted glass bulb with a stem carrying a scale. We read off the specific gravity from this scale according to the depth to which the instrument sinks in the liquid being measured. These results are decidedly crude but they are much used in many technical processes. The pycnometer is a more accurate instrument. Three forms are illustrated at a, b, and c in Fig. 19. a is a thin glass bottle, holding between 10 and 50 cm^3, with a ground glass stopper which terminates in a capillary tube. Weigh it empty, then full to the top of the capillary, first with water, then with the liquid to be

investigated, and from these results we may make our comparison. The form *b* is the most convenient we have. It is filled by suction. Holding a bit of filter paper to the fine jet at the left, liquid may be withdrawn until the meniscus in the capillary at the right stands exactly at the mark. Thus it is easy to secure equal volumes accurately. *c* shows a different apparatus recommended by Kohlrausch.

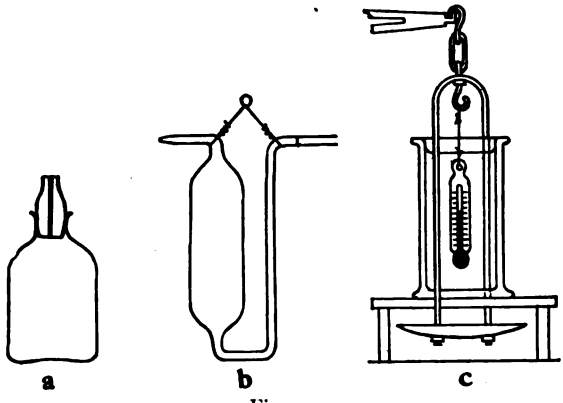


Fig. 19.

A glass "sinker," in which a thermometer is incorporated, is suspended from the balance and weighed, first in air, second in water, third in the liquid. From these weights the calculations follow readily. Kohlrausch obtained results correct to the sixth decimal place with this instrument.* The sinker may be made of quartz glass or platinum for use at high temperatures.

Effect of Temperature. It is a rule with but few exceptions that liquids expand with increase of temperature, but no regularity has been observed between the rates of expansion of different liquids, nor is there a simply formulated regularity in the rate of expansion of any one single liquid. For example, water decreases in volume from 0° to 4°, its temperature of maximum density. It expands four per cent of its volume when raised from 0° to 100°, and of these four per cent, one per cent occurs between 0° and 50°, and the other three per cent between 50° and 100°.

Specific Volume. Specific volume is the ratio between two volumes containing equal masses. If water be taken as the standard it is the reciprocal of the density.

* "Lehrbuch der Praktischen Physik," F. Kohlrausch, eleventh edition, 736 pp. (1910), p. 68.

Molecular Volume. In order to bring out any relationships which may exist between density and chemical constitution we must convert these arbitrary measures into terms expressed in our chemical units. We do this by the aid of what we call the molecular volume, *Vm*, the volume occupied by a molecular weight in grams, the specific volume times the molecular weight. For instance, the density of benzene, C_6H_6, at 0° is 0.9. Then its specific volume is $\frac{1}{0.9}$ and its molecular volume is $\frac{10 \times 78}{9} = 86.6+$. A molecular weight in grams of benzene at 0° occupies 86.6+ cm^3.

Corresponding Conditions. The question rises, at what temperature should comparisons be instituted. There is no obvious reason why the densities of substances as related to their chemical properties should be compared at 0° or 100° or any other point on the scale. H. Kopp (1817–1892) carried out a large number of experimental investigations and finally concluded to make the comparison at their boiling points. This was a fortunate choice, for much later, reasoning from van der Waals' equation, which is also called the "equation of conditions," we have developed what we call the theory of corresponding states (which will be discussed later), and according to this, chemical properties are best compared when substances are at temperatures which are equal fractions of the distance between the absolute zero and their critical temperatures. Now the boiling point of a substance (at 760 mm. pressure), on the absolute scale, has been found to be about two-thirds of its critical temperature, and so Kopp inadvertently, or instinctively, chose as we should choose to-day.

Kopp's Results. He calculated the molecular volumes of substances at their boiling points by extrapolation from determinations at lower temperatures. He found that metameric * substances have nearly the same molecular volume, and that equal differences in composition (such as the constant difference of CH_2 between successive members of a homologous series) correspond to nearly equal differences in molecular volumes.

He concluded that the molecular volume is an additive property, the sum of the volumes apparently occupied by the atoms.

Atomic Volumes within Molecules of Liquids. Kopp estimated what he called the atomic volume; *i.e.*, the volume occupied by one atomic weight of a substance, as follows:

* The distinction between isomer and metamer is not maintained, and isomer is generally used as if synonymous with metamer.

		V_m	Difference.
Formic acid.....	$HCOOH$	42	
			22
Acetic acid.....	CH_3COOH	64	
			22
Propionic acid.....	CH_3CH_2COOH	86	
			22
Butyric acid.....	$CH_3CH_2CH_2COOH$	108	

The table contains the molecular volumes of four acids in a homologous series. It will be noticed that an addition of CH_2 increases the molecular volume by 22 units in each case. Therefore the volume to be ascribed to the presence of this CH_2 is 22 units. Kopp next observed that when two atoms of hydrogen were substituted for one atom of carbon, the molecular volume of the compound was not changed. For example, cymol, $C_{10}H_{14}$ has a molecular volume of 187. Octane, C_8H_{18}, has a molecular volume of 187 and it may be considered as cymol diminished by two carbon atoms and increased by four hydrogen atoms. Then as CH_2 equals 22 and one atom of carbon occupies the volume of two atoms of hydrogen, the atomic volume of carbon may be said to be 11, and the atomic volume of hydrogen 5.5.

Knowing now these values, they may be subtracted from the molecular volume of a compound containing a third element and the remainder is the value to be ascribed to this third element. In this way Kopp calculated numerous atomic volumes.*

He observed variations in the atomic volume which appeared to be due to the position of the atom, to the way in which it was connected with other atoms in the molecule. Then the atomic volume is in this measure a constitutive property. He found that oxygen in the hydroxyl group has an atomic volume of 7.8, while oxygen doubly linked with carbon has an atomic volume of 12.2. Similar exceptions were found for other elements. He found also that 4.4 units should be added for each "double bond." This property may then be used as an argument for the presence or absence of a "double bond."

Hexahydro derivatives of benzene have a smaller molecular volume than isomeric olefines, *i.e.*, the formation of a ring results in a contraction of the molecule.

* The atomic volumes so derived, representing the relative space occupied within a liquid molecule, must not be confused with the atomic volumes discussed in Chapter VII, derived by dividing the atomic weight by the density of the solid element.

Additional work has demonstrated that these rules are not invariably applicable. The atomic volumes of all elements are more or less variable, and the molecular volume is partly additive and partly constitutive. Therefore we cannot formulate it satisfactorily. Traube says that these rules of Kopp do not apply because of association of molecules in the liquid state.

Covolume.* Traube believes we must distinguish between the volume occupied by the kernel of matter at the center of an atom, a somewhat compressible shell of luminiferous ether attached to this kernel, and another space out of which the atom keeps other atoms and within which it is free to vibrate. This additional space, occupied and defended by the atom, is called the covolume. The reasoning is applicable also to molecules, and the molecular covolume appears to be nearly a constant quantity for many substances.

Traube calculated a series of atomic volumes, much as did Kopp. For 0° he found: C = 9.85; H = 3.05; O = 5.5. The molecular volume of ethyl ether, $C_4H_{10}O$, at 0° is found experimentally to be 99.5. If we consider the molecular volume as the sum of the atomic volumes we have,

$$\begin{aligned} 4\,C &= 39.4 \\ 10\,H &= 30.5 \\ O &= \underline{5.5} \\ & 75.4 \end{aligned}$$

The difference, or $99.5 - 75.4 = 24.1$, is what is called the molecular covolume.

Application to Selecting Molecular Weights. Suppose, by analysis, a liquid is found to have the empirical formula C_2H_4O and that we find its specific volume at 0° is 1.073. If we assume C_2H_4O to be the correct formula, we have, $2 \times 12 + 4 + 16 = 44$ as the molecular weight, and the molecular volume is $44 \times 1.073 = 47.21$. Calculating the molecular volume as the sum of the atomic volumes, we have 2 C (19.70) + 4 H (12.20) + O (5.5) + covolume (24.1) = 61.5. There is not a good agreement between the results of the two methods of calculation. The next possibility is that the molecular formula is $C_4H_8O_2$. The formula weight corresponding to this is 88, and the molecular volume is $88 \times 1.073 = 94.42$. Calculating the sum of the atomic volumes we have, 4 C (39.4) + 8 H (24.4) + 2 O

* See "Ueber den Raum der Atome," by J. Traube. Sammlung Chemischer und chemisch-technischer Vorträge, edited by F. B. Ahrens, 4, 255–332 (1899).

(11) + covolume (24.1) = 98.9, a fair correspondence, better than would be obtained with the next possibility, $C_6H_{12}O_3$, and so the molecular formula is probably $C_4H_8O_2$.

Association. Traube has applied this method to a number of liquids, and his results indicate that many substances in the liquid state are associated; that they consist of molecules which are small multiples of the gaseous molecules of the same substance. His atomic volumes are to such an extent constitutive properties, varying according to the way the atoms are connected in the molecule, that the method cannot be said to be generally useful.

Compressibility. Liquids are decidedly incompressible, and different liquids are differently compressible. For example, an increase of one atmosphere in the pressure diminishes the volume of water 0.000 042 9 of its original volume, while the same increase in pressure diminishes the volume of ether 0.000 156 of its original volume.

T. W. Richards (1868–) has developed interesting considerations regarding the compressibility of liquids and solids and the "intermolecular" cohesion and "affinity pressure" of atoms within molecules. Lack of space prevents us from entering into a discussion of this topic.*

Surface Tension. The surface of a liquid has different properties from its interior and acts like an elastic bag tending to diminish the surface area. This is the obvious resultant of the mutual attractions of the molecules. The most familiar manifestation is the formation of drops. As a liquid comes slowly out from a small orifice, it hangs in a shape resembling a hemisphere at first. As more liquid comes out, it hangs down further and becomes pear-shaped. Finally the weight is sufficient to cause it to break loose as a sphere.

Soap Bubble Experiment. A striking experiment to demonstrate the fact that surface tension always tends to diminish the surface area may be shown by means of soap bubbles. A T-tube carries a small glass funnel or pipe bowl at the ends of two of its arms. A stopcock is in each of the three arms. Blow a small soap bubble on one funnel and a larger soap bubble on the other. Then turn the stopcocks in such a way that there shall be an open passage between

* T. W. Richards, *Zeitschr. f. phys. Chem.*, **40**, 169–184, and 597–610 (1902); **42**, 129–154 (1903); **49**, 1–14, 15–40 (1904); **61**, 77–99, 100–113, 171–182, 183–199, 449–454 (1908); **71**, 152–178 (1910); *Zeitschr. f. Electrochem.*, **13**, 519, 520 (1907); *Jour. Am. Chem. Soc.*, **26**, 399–412 (1904), and "Faraday Lecture," *Jour. Chem. Soc.* (London) **99**, 1201 (1911).

the two bubbles. The smaller bubble contracts, forcing its contents into the larger, for thus the total surface area is diminished. This is the reverse of what one would expect if surface tension acted like sheet rubber. The more a rubber bag is distended the greater the tension, and if two like rubber bags were attached to such an apparatus, the more distended bag would force a portion of its contents into the smaller until they were of equal size. This experiment illustrates that the surface tension of a liquid remains constant, (if temperature is constant), and always acts to diminish the surface area to a minimum.

Capillary Phenomena. The rise of liquids in small diameter (capillary) tubes and analogous phenomena are considered to be due to surface tension, and they are therefore utilized to measure it. When a glass plate is immersed in water, it is wet, and the water rises to a position *b*, as shown in Fig. 20, because in that way the total surface of the water is diminished.

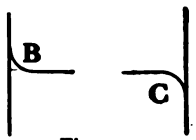


Fig. 20.

Capillary Depression. If the plate is not wet, as glass is not wet by mercury, there will be capillary depression, and the surface of the liquid will take up a position similar to that shown in the figure at *c*, for the same reason, because in this way the total surface is diminished.

It seems plausible to suppose there must be degrees of "wetting," and unlikely that a liquid either does not wet a solid at all or wets it as thoroughly as any other liquid would wet it. This question has not as yet been sufficiently investigated.*

Jurin's Law. For any liquid which completely wets the walls, the product of the radius into the capillary ascension is a constant. This is known as Jurin's law.†

Measure of Surface Tension. The weight of the liquid raised by capillary attraction is a measure of the surface tension. Denote the surface tension by γ. ~~This is~~ also called the capillary constant. γ equals the weight of the liquid raised by a plate of unit length, (one centimeter). If L equals the length of the plate in centimeters, the total weight, which we shall denote by P, is equal to γL.

* Feustel, *Annal. der Physik.*, **16**, 61 (1905).

† We have been learning in recent years to attribute many epoch-making discoveries to Leonardo da Vinci (1452–1519). Among these are the first recorded observations of capillary phenomena. The first quantitative relationship to be established was Jurin's law, announced in 1718. The theories and formulæ were developed by Laplace, Poisson, Gauss, and others.

Calculation of γ from Capillary Ascension. Suppose the inner diameter of a capillary tube to be $2r$. Let s equal the density (specific gravity) of the liquid, and we observe that it rises h centimeters. Then πr^2hs equals the weight of the liquid lifted. This is then equal to γL. Imagine the tube slit lengthwise, and unrolled, forming a flat plate. Such a plate will have the length $2\pi r$. Then $\pi r^2hs = 2\pi r\gamma$, and $\gamma = \frac{rhs}{2}$.

These calculations give correct results only if the meniscus shows an even curvature and is hemispherical, forming thus an angle of 0° with the walls. If this condition is not realized, if the angle made by the last portions of the liquid and the walls is θ, then $\frac{rhs}{2} = \gamma \cos \theta$.

Specific Cohesion. A value called the specific cohesion is another constant frequently used. It is denoted by the symbol a^2, and $a^2 = hr = \frac{2\gamma}{s}$.

Calculation from the Size of Drops. We may determine the capillary constants from a measurement of the size of the drops which form as the liquid slowly comes out from a small orifice. Count the number of drops obtained from a known volume and calculate the volume of one drop. The volumes of the drops are directly proportional to the heights to which the liquids would ascend in a capillary tube. Following is a table of values for a^2 and for γ for a few familiar liquids.

	a^2	γ
Water (0°)	15.40	7.70
Alcohol (0°)	6.06	2.58
Ether (0°)	5.43	1.97
Benzene (15°)	6.82	2.88
Chloroform (12.5°)	3.80	2.81
Olive oil	7.16	3.27*

* O. D. Chwolson, *Lehrbuch der Physik*, I, 599.

Experiments. The difference in surface tension between liquids may be demonstrated by simple but interesting experiments. For instance, place a thin layer of water on a level sheet of glass, then pour a little alcohol in the middle of the pool of water thus formed

The water, having the stronger "skin," pulls away to the sides, carrying the alcohol with it and leaving the center nearly dry for a short time.

A glass containing some sherry or other wine of about the same percentage alcohol shows a curious behavior illustrating the same phenomenon. If the glass be tilted in such a way that portions of it above the surface are wetted with the wine, it will be noticed that the even film breaks up into drops which appear to be attracting liquid from below until they grow so heavy they fall. The alcohol evaporates rather quickly from the film, and thus the remaining liquid contains less alcohol and more water, and therefore has a greater surface tension and draws up more of the wine. This proceeds until the drops have grown so heavy that by gravitation they fall.

The following is an eminently practical application of these simple principles. A solution of grease in benzene has a greater surface tension than pure benzene. If it is desired to remove a grease spot from some fabric, the pure benzene should be applied in a ring surrounding the stain. Then, as the grease dissolves in the benzene, furnishing a liquid with greater surface tension, it pulls away and so piles itself up in the center of this ring, and may be removed. If the pure benzene be poured in the center of the grease spot, the solution of grease in benzene forms a ring around pure benzene, and having the stronger "skin," pulls away, and thus the grease spot is converted into an ever-widening ring.

Surface Tension and Temperature. The surface tension diminishes as the temperature increases, and this diminution is almost proportional to the increase in temperature for any one liquid. It becomes equal to zero, and the meniscus disappears, at the critical temperature.*

Definition of Critical Temperature. We may then define the critical temperature of a substance as the temperature at which the surface tension between liquid and vapor becomes equal to zero, and any meniscus or bounding surface disappears.

Surface Tension and Mutual Solubilities. Water is soluble in phenol and phenol in water to a certain extent. These two solutions have different surface tensions, and in contact there is a meniscus between them. As we raise the temperature the difference between the surface tensions of these two solutions becomes less, and the meniscus accordingly flattens until, finally, it disappears. At the temperature at which this meniscus disappears, water and phenol are

* This is not strictly accurate.

miscible in all proportions. This temperature is known as the critical temperature of solubility.

Water and alcohol are miscible in all proportions. There is then no surface tension at the contact surface, rather a tendency, like that in gases, for each to occupy the largest possible volume. In this way we may convert the study of the mutual solubility of two liquids to a study of their surface tensions.

Surface Tension and Vapor Pressure. Vapor pressure is the name we give to the tendency shown by substances to pass from the liquid or solid state into the gaseous state. Surface tension evidently must act in opposition to this. Now if we have a very small drop of some substance, there are fewer molecules to attract those in the surface layer. Therefore the surface tension is less than it would be for a larger body of that substance. Therefore the vapor pressure is less neutralized, and a small drop has a greater tendency to volatilize than a large one. We may show this experimentally as follows: Melt some sulphur in a tube and distil until small drops collect in the upper portion. Those drops which were accidentally larger in the first place will continue to grow, at the expense of those which were accidentally smaller, until all of the sulphur has been accumulated in relatively few fairly large drops. The beginning of the process shows a large drop surrounded by a clear zone, because the small drops nearest the large ones are generally the first to disappear.

Surface Tension of Solutions. We know a good many cases where dissolving some substance produces but small alteration in the surface tension of the solvent. On the other hand many organic substances if present in mere traces in water exert notable effects. For instance, one part of caprylic alcohol in 30 000 parts of water has been detected from the lowering of the capillary constant it produces.*

Molecular Weights from Surface Tension. Let m equal the molecular weight in grams and s the density of a pure liquid at a given temperature. Then $\frac{m}{s}$ is the volume occupied by a molecular weight in grams; call this Vm. Count temperature downward from the critical temperature of the substance under investigation. Let τ

* From time to time certain regularities have been observed between the lowering of the capillary constant of a solution and the constitution or molecular weight of the solute. For instance, J. Traube stated, *Liebig's Annal.*, **265**, 27–55 (1891), that in dilute solutions the lowerings of the capillary constant of water by equimolecular quantities of members of some homologous series of organic compounds stand in the interesting ratio, $1 : 3 : 3^2$. . . .

equal the number of degrees centigrade below the critical temperature at which all observations are made. Determine γ at temperature τ. Eötvös* demonstrated experimentally that the relation $\gamma V m^{\frac{2}{3}} = k\tau$ for many substances, where k is a constant like the gas constant R, and has the numerical value 2.1 to 2.2. Ramsay and Shields† showed that the formula held better if the temperature is reckoned from a point about six degrees below the critical temperature and wrote the formula, $\gamma V m^{\frac{2}{3}} = k(\tau - \delta)$ where δ = about 6. The necessity of this correction indicates that the surface tension of a liquid becomes equal to zero a little before the critical temperature is reached.

The similarity between this formulation and the gas equation, $pv = RT$, is evident. The term $\gamma V m^{\frac{2}{3}}$ is composed of the intensity factor γ and the capacity factor $V m^{\frac{2}{3}}$. This latter term is proportional to the surface area of a sphere containing a molecular weight in grams.

Suppose we wish to find the molecular weight of a pure liquid. We determine its critical temperature by methods which will be described, and we determine s and γ at temperature τ. Substituting in the formula, $\gamma V m^{\frac{2}{3}} = 2.2(\tau - 6)$, we obtain a numerical value for $V m^{\frac{2}{3}}$ where Vm is the volume containing a molecular weight in grams. Knowing the density s we calculate the weight of this volume, and it is the molecular weight sought.

This method is rather important, inasmuch as it is the best we know as yet for obtaining molecular weights of pure liquids.

Numerous substances such as benzene, carbon tetrachloride, ethyl ether, carbon disulphide, benzaldehyde, nitrobenzene, and aniline give nearly the same results by this method as by vapor density methods. From this we may conclude the liquid molecules are the same as the gaseous, that polymerization does not occur with liquefaction.

Association. Other substances, particularly those containing hydroxyl groups, and organic acids, give molecular weights higher than those obtained by vapor density methods. We conclude that two or more molecules associate to form one upon liquefaction in these cases. We do not have to assume extensive polymerization. Acetic acid and water appear to consist of molecules represented by doubling the usual formulæ.‡

* *Wied. Annal.*, **27**, 452 (1886).

† *Zeitschr. f. phys. Chem.*, **12**, 433 (1893).

‡ For additional data see Eötvös and Ramsay and Shields, *loc. cit.*, Ramsay and Aston, *Zeitschr. f. phys. Chem.*, **15**, 98 (1894); Grunmach, *Drude's Annal.*, **15**, 401 (1904); Morgan and Stevenson, *Journ. Am. Chem. Soc.*, **30**, 360–376 (1908).

Internal Friction or Viscosity. Work must be done when liquid particles are pushed past each other, and the amount of work necessary depends upon the internal friction or viscosity of the liquid.

Coefficient of Viscosity. The coefficient of viscosity or internal friction is defined as equal to the work required to push two surfaces of one square centimeter area past each other in parallel directions a distance equal to their distance apart in one second. It is denoted by η.

Experimental Measurement. The measurement of the coefficient of viscosity is most conveniently carried out by Poiseuille's method, in which the rate of passage of the liquid through capillary tubes is determined. It has been proved experimentally, and it has been deduced theoretically, that when liquids flow through capillary tubes the following formula holds: $\eta = \frac{p\pi r^4 t}{8 v \tau}$, wherein η is the coefficient of viscosity; r is the radius of the tube; π has its usual value, 3.141 59; τ is the length of the tube; v is the volume of liquid which passes through in t seconds. This formula applies only when the diameter of the tube is small and its length is above a definite minimum depending on that diameter.

Viscosimeters. Instruments used to determine the viscosity of a liquid are called viscosimeters. One of the simplest and most convenient is as follows: A tube very like a small pipette, with a bulb between two small bore tubes, on each of which is a mark, is sealed onto a length of fine capillary tubing. The whole is filled with the liquid to be investigated and placed in a thermostat. A definite pressure is applied, forcing the liquid out through the capillary. The time is measured which is required to empty the instrument from the mark above the bulb to the mark beneath it.

Another method is that of Coulomb and Maxwell, who determined the force required to hold one cylinder stationary while they rotated uniformly a coaxial cylinder, the space between the two being filled with the liquid. Coulomb, Maxwell, and O. E. Meyer measured the logarithmic decrement of a horizontal disk hung as a torsion pendulum, rotating first one way then the other, over a fixed parallel disk, the space between being filled with the liquid. Stokes measured the logarithmic decrement for a pendulum oscillating in the liquid. Helmholtz measured the logarithmic decrement of a sphere vibrating about one diameter in an " ocean " of the liquid, that is, in an

amount so large the influence of the walls of the container might be neglected. He also reversed this principle, rotating a hollow sphere filled with the liquid. These methods give values for what we may describe as the absolute viscosity.

If equal volumes of two liquids are caused to flow out of the same apparatus under the same conditions of temperature and pressure, the times required, t_1 and t_2, must be directly proportional to the viscosities, η_1 and η_2; or $\eta_1 : \eta_2 = t_1 : t_2$. Expressing the values in Poiseuille's formula in the C. G. S. system, values of η for water are as follows: *

0°	0.01778	60°	0.00468
10°	0.01303	70°	0.00406
20°	0.01002	80°	0.00356
30°	0.00798	90°	0.00316
40°	0.00654	100°	0.00283
50°	0.00548		

Using these values and the above proportion, viscosities of other liquids may be determined with ease.

Specific Viscosity. By specific viscosity is meant a comparison between the viscosity of the liquid under investigation and that of some liquid chosen as a standard. One form of this comparison often used is the time required for a given volume of the liquid to flow out of some suitable aperture at a chosen temperature, multiplied by one hundred, and divided by the time required for an equal volume of water at 0° to flow out of the same apparatus.

Lubrication. The practical importance of a knowledge of viscosity of liquids is apparent when we realize that the whole problem of lubrication is one of internal friction of the lubricant. If the conditions are ideal, there is a liquid layer between the metals, which are then not in contact at all, and the friction is wholly a question of the viscosity of the liquid. Other things being equal that oil with the least viscosity should be chosen.

Temperature Coefficient of Viscosity. The coefficient of viscosity of a liquid diminishes rapidly with increasing temperature. For example, the viscosity of water at 80° is but one-third of its value at 10°. Poiseuille formulated the connection between the viscosity coefficient and the temperature as $\eta_t = \frac{\eta_0}{1 + \alpha t + \beta t^2}$ wherein η_0 and η_t are the viscosities at 0° and at temperature t, and α and β are

* Landolt-Börnstein-Meyerhoffer, "Tabellen," p. 77.

constants, different for different substances. Slotte* suggested the formula $\eta = \frac{C}{(1+bt)^n}$ where η is the coefficient of viscosity at the temperature t, and C, b, and n are constants depending on the nature of the liquid. Thorpe and Rodger† found this expression formulated the facts fairly well. The following table contains some of the values they obtained for C, b, and n.

Substance.	C.	b	n
Water	.017944	.023121	1.5423
Chloroform	.007006	.006316	1.8196
Carbon tetrachloride	.013466	.010521	1.7121
Carbon disulphide	.004294	.005021	1.6328
Acetic acid	.016867	.008912	2.0491
Ethyl ether	.002864	.007332	1.4644
Benzene	.009055	.011963	1.5554
Toluene	.007684	.008850	1.6522
Methyl alcohol	.008083	.006100	2.6793
Ethyl alcohol	.017753	.004770	4.3731
Propyl alcohol	.038610	.007366	3.9188

Viscosity and Pressure. The viscosity of water diminishes slightly as the pressure is increased while that of benzene and ether increases with increased pressure.

Viscosity and Constitution. Many attempts have been made to establish some connection between viscosity and the constitution of the molecule. In a homologous series the substances with the higher molecular weights have greater viscosities. Metamers often have different viscosities. A substance with a "double bond" has greater viscosity than another of the same molecular weight but without a "double bond."

Viscosity of Salt Solutions. Arrhenius‡ showed that solutions of some salts, for instance potassium iodide and ammonium chloride, have less viscosity than pure water and that solutions of other salts have more. As the viscosity of the solvent must have much effect upon the motions of ions in the solution, and this in turn must have an effect on the conductivity, many researches have been carried out to establish connections between these quantities and the degree of dissociation. The conclusion has been reached that each ion is

* *Wied. Annal.*, **20**, 257, 557 (1883).
† *Phil. Trans.*, **185** A, 397 (1894).
‡ *Zeitschr. f. phys. Chem.*, **1**, 208 (1887).

surrounded by a coat or atmosphere of the solvent which moves with it.*

In some cases the viscosity of a solution has been found to be a maximum at a particular concentration. No simple laws connecting the viscosity with the concentration have been discovered. Some conclusions are perhaps deducible regarding the formation of hydrates in solution.

Viscosity of Gases. The viscosity of a gas is independent of the pressure but increases as the temperature increases. These facts, not what one would expect, may be deduced from the kinetic theory of gases.†

* The reader is referred to "The Relations between Chemical Constitution and Some Physical Properties," by Samuel Smiles, 583 pp. (1910), for a thorough discussion of this subject and many references.

† "Properties of Matter," by Poynting and Thomson, p. 217.

CHAPTER XIV

INDEX OF REFRACTION

THE index of refraction, n, was defined in Chapter VIII. Since it is different for light of different wave lengths we must use homogeneous light when measuring it. The most convenient source, and the most used, is the sodium lamp. A few bits of fused sodium chloride held by a platinum spiral in the bunsen flame serves the purpose well. Another much used light is the red line of the hydrogen spectrum. All values given in this chapter refer to sodium light.

Refractometers. Accurate measurements of the index of refraction are made with the spectrometer, a spectroscope on which prisms of different materials, or a hollow prism to hold liquids, may be mounted. The Abbé refractometer is another useful instrument, but the Pulfrich refractometer* is the only one ordinarily used in chemical investigations, and we shall therefore confine our attention to it.

Pulfrich Refractometer. The working parts of Pulfrich's refractometer are shown in Fig. 21. It consists of a glass prism P of high index of refraction with two faces exactly at right angles to each other, mounted on a substantial iron stand in such a way it may be taken off and cleaned and then returned to exactly the same position. The edges of the upper face are ground off, as indicated in the diagram, so that a glass cell, about 1.5 centimeters in diameter, may be cemented on, and yet none of the cement project as high as the clear glass surface. The liquid to be investigated is put in this cell. A lens about 8 cm. in diameter, carried by an arm

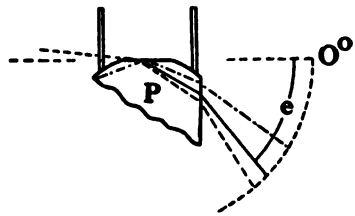


Fig. 21.

* Pulfrich, *Zeitschr. f. Instrumenten Kunde*, 8, 47 (1888) and 15, 389 (1895). *Zeitschr. f. phys. Chem.*, 18, 294 (1895). Also, "Das Totalreflectometer." 144 pp. (1890).

attached to the stand, gathers light from the source and sends a bundle of rays through the cell wall and liquid over the horizontal surface of the prism. A small reading telescope with cross hairs in the ocular is mounted on a graduated circle, and may be so moved as to look at the perpendicular face of the prism from different angles. As it is moved, a vernier travels over the graduated circle, and thus the angle at which it stands is read with accuracy.

If the telescope is in such a position that the observer is looking along the line indicated by dashes in the figure, he will see the light which comes from the source. It is refracted when it enters the horizontal face, and again when it leaves the perpendicular face, as indicated by the continuations of that line of dashes. As he rotates the telescope upward he will still see a bright field until his telescope is looking along the full line in the figure. This is the last ray he can see. Considering it as starting from the observer, it comes out parallel to the horizontal face, and thence goes to the source. If he rotates the telescope to a yet smaller angle, a position indicated by the dot and dash line, such a ray cannot get out of the prism, but is totally reflected from the horizontal face, and is lost in the mounting of the prism. The observer sees nothing. There is thus a field of light and a field of darkness, and the boundary is well defined. The telescope is adjusted with a micrometer screw so that this boundary exactly touches the point where the hairs cross, and the angle, e in the figure, is read. This boundary corresponds to the last ray which can get into the prism, and it came from the source in a direction practically parallel to the horizontal surface.

Formula. The index of refraction of the substance in the cup with reference to air is $\sqrt{N^2 - \sin^2 e}$ where N is the index of refraction of the glass of the prism, known and given with the instrument, and e is the angle determined as just explained. With the instrument come tables of the values for $\sqrt{N^2 - \sin^2 e} = n$, corresponding to values for e.*

* This relation is not immediately obvious and students cannot understand how we determine the index of refraction, air to substance, when the ray passes perpendicularly from one to the other. Therefore it is desirable to give the elementary physics and calculation involved. Suppose a ray of light passes from air through a horizontal layer of substance, then through a horizontal layer of glass, then out to air again. Its course is as indicated in Fig. 22. That its direction when back in air again is the same as its original direction is a fundamental, well-known fact. Then $e = e$. Of course $r = r$ and $i = i$ in the figure. The index,

Usefulness of the Value. Very little liquid is required, for the layer in the cup need be only enough to cover the horizontal face of the prism; it is not altered in any way and may be recovered with small loss, sometimes an important consideration. The determination is rapidly made and accurate. The index of refraction is a characteristic numerical value for a substance like the melting point, boiling point and specific gravity. For all these reasons it should be more generally used than it is, as a means of identification. At present its practical applications are mainly in the testing of essential oils and in the analysis of solutions for the presence of otherwise difficultly differentiated, complicated, organic compounds.

Le Blanc's Method for Solids.* The Pulfrich refractometer may be used to determine the index of refraction of a solid in case the solid is isotropic, that is, either amorphous or crystallizing in the first system. We use two liquids, one of low index of refraction, such as

air to substance, is $\frac{\sin e}{\sin r}$. We know the index of air to glass (prism), $\frac{\sin e}{\sin i} = N$. The index, prism to substance, is $\frac{\sin i}{\sin r}$. Multiplying index, prism to substance, by index, air to prism, gives us $\frac{\sin e}{\sin i} \times \frac{\sin i}{\sin r} = \frac{\sin e}{\sin r}$, the value we want.

Now consider the passage of the ray when the glass layer is a right-angle prism as indicated in Fig. 23. Index, air to prism, is again $\frac{\sin e}{\sin i} = N$. Index, prism to

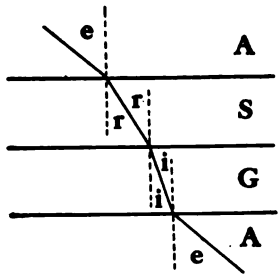


Fig. 22.

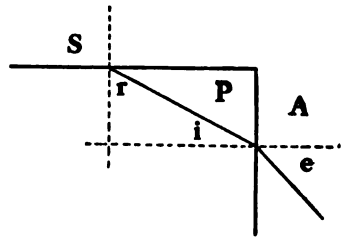


Fig. 23.

substance, is $\frac{\sin r}{\sin 90^\circ}$ because the last ray travels horizontally along the prism surface in the substance. Sin 90° = 1. Then index air to substance is $\sin r\, N$. $\sin r = \cos i = \sqrt{1 - \sin^2 i}$. Since $\frac{\sin e}{\sin i} = N$, $\sin i = \frac{\sin e}{N}$. Substituting,

$$\sin r\, N = N\sqrt{1 - \frac{\sin^2 e}{N^2}} = \sqrt{N^2 - \sin^2 e} = n.$$

* *Zeitschr. f. phys. Chem.*, 10, 433 (1892).

acetone, and one of high index of refraction, such as bromonaphthalene, the two miscible in all proportions. The powdered solid is suspended in a mixture of these two liquids in the cup of the instrument. If the index of the liquid is greater than that of the solid, we see a bright band across the field in the telescope. If the index of the liquid is less than that of the solid, the boundary is indistinct. The boundary is well defined only when the index of the liquid is exactly the same as the index of the solid. By adding now a little acetone, now a little bromonaphthalene, we may vary the index until we get this condition, and the measurement with the instrument then gives us directly the index of refraction of both liquid mixture and suspended solid.

Specific Refraction. The index of refraction decreases with increase of temperature, and therefore we should determine the temperature at the same time that we determine the index. But it has been found that this change in the index nearly parallels the change in density from the same cause. If n is the index (air to substance), and d the density at the temperature of measurement, $\frac{n-1}{d}$ is a nearly constant quantity for any one liquid. It is denoted by R, and is called the specific refraction. This is a poorly chosen name, for the value is not a relation existing between two quantities of the same kind, and the term " specific " should properly be reserved for such relations.

Lorentz and Lorenz Formula. Two independent investigators, of nearly the same name, almost simultaneously, published another formula. Lorentz,* starting from the electromagnetic theory of light, and Lorenz† from the undulatory theory, reached the same result. The fundamental premise in each case is that the index of refraction of a substance is a function of the volume actually occupied by the molecules. They concluded that the value $\frac{n^2-1}{n^2+2}\times\frac{1}{d}$ should be a constant, not only independent of the temperature, but even of the condition of aggregation of the substance. The deduction has been verified by experiment and is therefore to be preferred as an expression of " specific " refraction to the older formula, as is shown by the following table:

* *Wied. Annal.*, 9, 641 (1880).
† *Wied. Annal.*, 11, 70 (1880).

	$\frac{n-1}{d}$.		$\frac{n^2-1}{n^2+2}\times\frac{1}{d}$.	
	Vapor.	Liquid.	Vapor.	Liquid.
Water	0.3101	0.3338	0.2068	0.2061
Ethyl alcohol	0.4238	0.4583	0.2825	0.2804
Ethyl ether	0.4602	0.4935	0.3068	0.3026
Benzene	0.4880	0.5692	0.3253	0.3347 *

* Brühl, *Zeitschr. f. phys. Chem.*, 7, 1-33 (1891).

Molecular Refraction. Landolt, in order to bring out the chemical significance of the property, introduced another factor. He multiplied the specific refraction by the molecular weight, and the result which he thus obtained he called the molecular refraction. If we indicate the molecular weight by m and the molecular refraction by R_m, then $R_m = \frac{m}{d}\times\frac{n^2-1}{n^2+2}$.

The same difference in formula gives the same difference in molecular refraction, as is shown in the following table:

	R_m	Difference.
Formic acid	8.54	
		4.42
Acetic acid	12.96	
		4.50
Propionic acid	17.46	
		4.64
Butyric acid	22.10	
		4.69
Valerianic acid	26.79	

Metameric compounds are found to have nearly the same molecular refractions.

Atomic Refraction. A partially successful attempt has been made to ascribe a certain definite effect to each atom in a compound, in such a way that the index of refraction of the compound may be calculated as the sum of the effects of the individual atoms. But it has been found that one and the same atom has different effects depending on the way in which we suppose it to be attached in the molecule. The property is then not purely additive, but in a measure constitutive also. By comparing the molecular refraction of substances whose formulæ differ by one carbon atom, the value 2.501 has been obtained for carbon. In similar ways the following "atomic" refractions have been selected: hydrogen, 1.051; "hydroxyl" oxygen,

1.521; "ether" oxygen, 1.683; "carbonyl" oxygen, 2.287; chlorine, 5.998; bromine, 8.927; iodine, 14.12.

From these values we may calculate molecular refractions. Acetone is C_3H_6O and we have

$$3\,C\,(3 \times 2.501) + 6\,H\,(6 \times 1.051) + 1\,\text{carbonyl}\,O\,(2.287) = 16.096.$$

Actual observation gives 16.09.

What we symbolize by a "double bond" has an effect of its own, equal to 1.707, and as many times this value as there are "double bonds" must be added in such summations as this. It is evident that this relationship may be applied as an argument for or against the presence of such a combination in disputed or doubtful cases.

Atomic Refraction and Atomic Weight. In general, the greater the atomic weight the greater the atomic refraction, but the atomic refraction increases more slowly than the atomic weight, and we have not formulated the numerical relationship. Still, we could foretell that a lead glass must have a high index of refraction.

The property is partly additive and partly constitutive, and the facts we have established are practically reproductions of those we found in our consideration of molecular volumes. This confirms the view of Lorentz and Lorenz that the index of refraction is a function of the volume actually occupied by the molecules.

CHAPTER XV

SOLIDS

Properties of Solids. Solids differ from liquids in having definite shapes. Applying our kinetic theory we imagine their molecules as more firmly held together by mutual attractions than are the molecules of either gases or liquids.

Nothing Absolutely Solid. A candle or a stick of sealing wax, supported at one end in a horizontal position, bends rather rapidly; a glass rod in similar position does likewise, but more slowly. This is "flowing" in the same sense we say liquids flow; the difference is only in the rate. A good thermometer is exhausted before sealing. Atmospheric pressure upon the bulb gradually diminishes its volume, and this shows itself in higher readings of the instrument for a definite temperature as it grows older. Rocks "flow" under pressure in the course of geological ages.

Viscosity and Elasticity. The degree of viscosity of a substance is the property ordinarily thought of in determining whether a substance shall be called a solid or not; but we may select a series of substances such that they show a steady gradation from the most mobile liquids to the most rigid solids. Elasticity is another criterion. The body which returns most promptly and exactly to its original shape after a deformation is the most perfect solid. But we saw, in our consideration of the kinetic theory of gases, that any substance may be considered as perfectly elastic if the deformation is minute enough.

Two Classes of Solids. We may subdivide the substances commonly called solids into two classes, amorphous and crystalline. We imagine the molecules in an amorphous solid to be without definite order, much as we imagine them in liquids, only unable to move freely. An amorphous solid may then be considered as a liquid of great viscosity. In crystalline solids, however, we imagine that the molecules are in some orderly arrangement, and that this arrangement, in conjunction perhaps with the shapes of the molecules themselves, determines the crystal form.

In favor of these views is the fact that heating an amorphous body it gradually becomes more plastic, until at last we certainly must call it a liquid. But it shows no definite melting point, below which we can say that the substance is a solid and above which we can say it is a liquid.

On the other hand, heating a crystalline solid, we get an abrupt change at a definite temperature. It has a definite melting point. According to our kinetic theory, at this point the heat vibrations are extensive enough to shatter the orderly arrangement.

Crystallography. Crystalline solids occur in definite geometric forms and their study is crystallography. These forms are characteristic for different substances and often offer an exceptionally quick and convenient means of identification.*

Classification of Crystals. Crystal forms are classified according to the number of planes of symmetry which may be drawn within the crystal. There are thirty-two classes and no more are possible.

The older plan was to classify according to systems of axes. Weiss, in 1809, originated this classification, imagining axes within a crystal such that the crystal surfaces are more or less symmetrically arranged about their ends. He found that the countless different forms could all be considered as belonging to one or the other of six systems.

Weiss' Six Systems. We have:

First, the regular system: three axes, all of equal length and all making right angles with each other.

Second, the tetragonal system: two axes of equal length and the third axis either longer or shorter, but all three making right angles with each other.

Third, the hexagonal system: three axes of equal length crossing each other at angles of 60° and a fourth axis, either longer or shorter, at right angles to the others.

Fourth, the orthorhombic system: three axes of unequal length but all forming right angles with each other.

Fifth, the monoclinic system: three axes of unequal length, two of which cross at right angles, while the third is at right angles to one and not to the other.

* Microchemical analysis is an interesting branch of our science. See "Anleitung zur Mikrochemischen Analyse," by H. Behrens, 242 pp., second edition (1899), and "Mikrochemische Analyse der Wichtigsten organischen Verbindungen," by the same author.

Sixth, the triclinic system: three axes of unequal length but no right angles.

Hemihedry and Tetartohedry. Some crystals show only half the number of faces belonging to the perfect form. These are called hemihedral forms. Others, called tetartohedral, show only one-fourth the number of faces of the perfect form. Yet others, called ogdohedral, show but one-eighth the number of faces of the perfect form.

The First Law of Crystallography. In 1669 N. Steno (1638–1686) observed the fact that the angle between two given faces of a crystal is always the same for one substance, no matter what the size of the crystal or the conditions under which it was formed. The fact that there is a characteristic and constant angle for each crystalline substance is generally known as the first law of crystallography. It is a valuable means of identification and is much used for the purpose by mineralogists and occasionally by chemists.

Goniometer. The instrument used to measure this angle is called a goniometer. There are several forms: one, the reflection goniometer, consists essentially of a turntable with degrees marked on the circumference, and an observing telescope. The crystal to be measured is mounted in the center of the table and an object at a distance, reflected from one surface of the crystal, is brought to correspond to cross hairs in the ocular of the telescope. The turntable is then revolved until the same object is seen again in the same position, reflected in the adjacent crystal surface. From the number of degrees through which the crystal must be turned, the angle made by the two crystal surfaces is readily calculated.

Isomorphism. Several substances may crystallize in the same form, the characteristic angles, while not accurately the same, being nearly so. They are called isomorphous. Inasmuch as there is not identity of form, but close similarity, Ostwald suggested that homeomorphous is a better term than isomorphous.* E. Mitscherlich (1794–1863), in 1819, discovered the phenomenon in the potassium and sodium phosphates and arsenates. He observed that chemically similar elements and chemically similar compounds showed it, and it has been of use in selecting symbol weights from a series of possibilities, and in constructing the periodic table.

* $MgSO_4\,7\,H_2O = 89°\,26'$,
$ZnSO_4\,7\,H_2O = 88°\,53'$,
$NiSO_4\,7\,H_2O = 88°\,56'$.

Isomorphism of Elements. Sometimes one element in a compound may be replaced by another without altering the crystal form. For example, arsenic may replace phosphorus in sodium hydrogen phosphate, $Na_2HPO_4.12\,H_2O$, to form the arsenate, $Na_2HAsO_4.12\,H_2O$, and the characteristic angle of the original crystal is not altered. Since many compounds of arsenic are isomorphous with the corresponding compounds of phosphorus, the elements themselves are called isomorphous. When so called, one is not expected to infer that the pure elements necessarily crystallize with the same angle. It is a curious fact that chemists lay most stress on the angle measurement, while crystallographers lay most stress on the similarity of the chemical properties or formulæ.

Test for Isomorphism. The best test for the existence of isomorphism is to determine whether or not a crystal which has begun to grow in one solution will continue to grow in a saturated solution of the other substance; that is, whether the two substances will form mixed crystals, which do not contain the constituents in stoicheiometric proportions.

Isomorphism and Analysis. If we have a crystalline precipitate of one substance coming out of a solution containing an isomorphous substance, to some extent at least, we shall obtain mixed crystals; our precipitate will not be pure. Such conjunctions should be avoided in analytical processes.

Polymorphism. In many cases the same substance appears in two or more crystal forms. This phenomenon is called polymorphism. If a substance exists in two forms it is called dimorphous, if in three, trimorphous.

Sulphur occurs as orthorhombic crystals and as monoclinic crystals, also in two amorphous varieties, one of which is soluble in carbon disulphide, the other is not. Calcium carbonate occurs as the mineral calcite in a subdivision of the hexagonal system known as rhombohedral, and also as the mineral aragonite in the orthorhombic system. Carbon as charcoal is amorphous, as graphite it is in the monoclinic system although the form appears closely to resemble a hexagonal form; diamonds are in the regular system.

The phenomenon of polymorphism is very general and microscopic crystallographic investigations of organic compounds particularly reveal it with unexpected frequence.

Properties of Crystals. All crystals but those in the first or regular system show differences in properties dependent upon the

direction within the crystal in which the measurement is made. For instance, they conduct heat and electricity best in certain directions. Elasticity and hardness, and practically all measurable physical properties, are found to have different values in different directions.

Isotropic and Anisotropic Substances. Light passes through crystals of the first system and through amorphous bodies at the same rate in any direction. They are called isotropic. Through crystals of all other systems it passes at a maximum rate in one direction, and at a minimum rate in a direction at right angles to the first. Such substances are called anisotropic. Glass may be made to become anisotropic by pressure, mechanically applied, or resulting from quick cooling. Optical methods are used to reveal strains in the interior which would unfit glass for certain uses.

Double Refraction. If we look at a dot on a sheet of white paper through a piece of iceland spar ($CaCO_3$) we see two dots. This phenomenon is due to what is called double refraction. Our plausible explanation is as follows: Let us form a mental picture of the structure of a ray of light with that definiteness we find so useful in reasoning about atoms and molecules. Cut a cross section of a single ray coming directly at us. We may think of it as consisting of many electrons moving in a great variety of directions in a plane perpendicular to the direction in which the light is moving. We may picture some of them as vibrating to and fro on almost every radius which can be drawn through the center of the ray, some describing circular, others elliptical orbits around the center. The total effect is an equal amount of disturbance to an equal distance in every direction in that plane. Or we may adopt the undulation theory and think of luminiferous ether instead of electrons vibrating in all these directions. The picture is much the same if we imagine particles of luminiferous ether, but it is a little awkward to think of the ether as made up of particles and as continuous, simultaneously. We may imagine we have pasted small gum labels on the continuous ether, then these will be engaged in the intricate dance.

Polarized Light. Now when that ray enters an anisotropic substance, we conceive it finds it easier to vibrate in two planes at right angles to each other than in other planes. These variegated vibrations are thus resolved into two main planes.* If this resolution is complete we say the light is completely plane polarized. We have

* In the phraseology of the electromagnetic theory, the magnetic vibrations occur in one plane and the electrical in a plane perpendicular to the first.

occasion in some cases to imagine the nature of a substance such that the easiest form of vibration is in circular paths, and that the vibrations are resolved into the describing of circles. We then call the light circularly polarized; in similar way we imagine elliptically polarized light consisting of vibrations in ellipses.

In our work we need consider only completely plane polarized light, vibrations at right angles to each other and to the line of flight. Vibrations in one of these planes proceed more rapidly through the anisotropic substance than those in the other. The angle through which a ray is bent (refracted) is greater the slower it goes. Therefore one ray is split into two and we have double refraction, seeing two dots where there is but one.

Optical Axes. This splitting of one ray into two is effected by every substance that is not isotropic, but it is more pronounced with iceland spar than with most other substances. All anisotropic substances have either one or two (no more) directions in which this splitting does not occur. These directions are called the optical axes. When there are two they usually make a rather small angle with each other.

Nicol Prism. Two wedge-shaped pieces of iceland spar are cut as shown in Fig. 24 and cemented together with Canada balsam. This combination is called a Nicol prism from William Nicol (1768–1851), a Scotchman who invented it in 1828. A ray of light upon entering is split into two, one called the ordinary, the other the extraordinary ray, both completely plane polarized. They impinge upon the cemented surface at such an angle that the ordinary ray is totally reflected and lost in the mounting of the prism, while the other passes through. Thus the light which comes out of the other end is plane polarized.

Fig. 24.

Polariscope. If light, polarized by passing through one Nicol prism, strikes another, it will pass through undiminished in intensity provided the screening effect of the second is parallel to that of the first. If the screening effect of the second Nicol prism is perpendicular to that of the first, no light passes. We say the nicols are " crossed."

A polariscope consists essentially of two Nicol prisms. The one through which the light first passes is called the polarizer, and that nearest the eye of the observer, through which the light passes last,

is called the analyzer. The substance to be investigated is placed between the two.*

Crystals in Polarized Light. An anisotropic substance inserted in a polariscope between crossed nicols produces effects which enable us to tell much regarding the crystal form.

Crystals in the tetragonal and hexagonal system have but one optical axis. If a plate is cut perpendicular to this axis and is observed between crossed nicols, we see a dark center surrounded by concentric rings, the whole shot through by two dark bands crossing at the center. If monochromatic light, as from a sodium lamp, is used for these observations, the rings alternate light and dark. If white light is used, owing to the fact that different wave lengths are differently refracted, there is a play of colors. Upon turning the analyzer through 90° every color changes to its complementary color and the dark cross becomes a light cross.

Crystals in all other systems (excluding the regular which is isotropic) have two optical axes. If a plate is cut perpendicular to the bisector of the angle between these axes and is observed with monochromatic light between crossed nicols, we see two dark centers surrounded by dark and light circles. Outside of these, light and dark bands follow the contour to include both centers and give a figure something like a pair of spectacles. Two dark bands, opposite branches of an hyperbola, cut through the picture, each including one center. These bands are symmetrically placed in such a way they are nearest each other at these centers. In particular cases, in place of these curves, we may have a dark cross, the center of which is between the centers. The change, upon rotating the analyzer through 90°, is analogous to that described for crystals with one optical axis; every color changes to its complementary color.

An isotropic substance produces no effect unless it happens to be one of the relatively few substances which rotate the plane of polarized light.

Rotation of the Plane of Polarized Light. If a thin plate of quartz is inserted between the crossed nicols, and is examined with monochromatic light, the whole field becomes lighter, but by rotating

* Plates cut from tourmaline crystals plane polarize light and absorb in great measure the vibrations in one plane. Thus two such plates form a polariscope, somewhat crude, but nevertheless useful in many crystallographic investigations. Light may also be polarized by reflection at the "polarization angle" (about 56°) from glass plates. But none of these devices equal in usefulness the Nicol prism described in the text.

the analyzer through an angle, the field is made as dark as before. The plausible explanation is that the plane in which the light coming from the polarizer is vibrating, is rotated as it passes through the quartz. The angle through which the analyzer must be turned, to reëstablish the previous darkness, is thus a measure of the rotation produced by the quartz. The analyzer is mounted in the center of a disk, graduated in degrees, and a vernier enables us to measure the angle accurately.

Right and Left Rotation. If it is necessary to rotate the analyzer in the direction of the hands of a watch, the substance is called right rotating, or dextrorotatory; if in the opposite direction, it is called left rotating or lævorotatory.

This ability to rotate the plane of polarized light is possessed by only a few solids; quartz is the most notable example, sodium and potassium chlorate crystals are others. A larger number of pure liquids have this power. For instance, German, French, and Venetian turpentines rotate the plane to the left, while Austrian turpentine rotates it to the right. Pinenes and amyl alcohol are other examples. A still larger number of substances in solution rotate the plane of polarized light, and it is in the study of solutions that the polariscope finds its most important applications. We shall consider these applications in detail in Chapter XVII.

Inferences from Crystal Forms. There can be no manner of doubt but that these various crystal forms are manifestations of an orderly internal arrangement, and that they are so many clues to the shapes and arrangements of the molecules. Suggestions in great variety have been made ever since the time of R. J. Haüy (1743–1822), who founded the science of crystallography.*

"Etch Figures." Even the solubility of a crystal is different in different directions. If the polished surface of a crystalline substance

* A presentation of these theories, to be of value, must be somewhat extended, and the reader is therefore referred for further information to works on crystallography. Recent views of interest to chemists are contained in articles by L. Sohncke, *Zeitschr. f. Krystallographie*, **13**, 209–214 (1887); **14**, 417–426 (1888); **19**, 529–559 (1891); **20**, 445–467 (1892).

W. Barlow and W. J. Pope, *Jour. Chem. Soc.* (London), **91**, 1150–1214 (1907), draw conclusions regarding the volumes of atoms and valence, from crystalline forms. A summary of these conclusions and additional references are contained in the article on crystallography by W. J. Pope, in "Annual Reports" of the Chemical Society (London), **5**, 258–279 (1908). See also "An Introduction to Chemical Crystallography," by P. Groth, translated by H. Marshall, 123 pp. (1906).

is treated for a brief time with a solvent, some parts dissolve faster than other parts, and geometrical patterns in faint relief result. From these the crystal form may be determined. Polished surfaces of steel, other metals and alloys, may be so "etched" with different solvents. The process reveals, not only the crystalline form, but also the presence of different substances (martensite, cementite, etc.) in the steel. By observing these under a microscope, much may be learned regarding the heat treatment to which steel has been subjected. This information is as important as, and may be more important than, that obtained by chemical analysis. These methods are new, and as they are fairly rapid they are destined to have increasing applications.

Liquid Crystals. We know a curious group of organic liquids which partake somewhat of the character of solids. Cholesteryl benzoate, a solid at ordinary temperatures, melts at 145.5° to a cloudy liquid, which may be poured from vessel to vessel like any other liquid. And yet, examined between crossed nicols, it shows the phenomenon of double refraction. As has been made evident in the earlier part of this chapter, this phenomenon indicates that light passes more rapidly in one direction than another, and this we associate with an orderly arrangement of particles such as gives rise to crystal forms. We might suppose this was exclusively a property of solids and that liquids must of necessity all be isotropic.

The only assumption possible is that in this strange liquid the molecules are held in an orderly arrangement. At 178.5° the cloudy liquid clears up, and no longer exhibits the ability to doubly refract light. The substance has thus two definite melting points, at 145.5° and at 178.5°, and between these temperatures may properly be said to consist of liquid crystals.

Ammonium oleate and the sodium salt of α naphthylamine sulphonic acid, and other substances show the same behavior. These phenomena were first discovered by O. Lehmann.*

After the novelty of the idea has worn off a little, it is by no means incomprehensible. The forces holding particles in definite position can easily be imagined as grading off gradually until they are so weak the substance will fill completely the lower part of a containing vessel, and yet not so weak but that the rather mobile particles assume definite positions in relation to each other. We have, in the malleable metals, what we might consider as the reverse of this picture. Many of these, like gold, are crystalline in structure, and yet may be pounded

* *Zeitschr. f. phys. Chem.*, 4, 462–472 (1889).

into any shape, that is, they have plasticity, a property particularly characteristic of a liquid.

Molecular Volumes of Solids. The atomic volume of solid elements was defined and shown to be a periodic function of the atomic weight in Chapter VII. Efforts have been made to establish connections between these and the molecular volumes* of solid compounds with but little success.

Some of the results are rather unlooked for. For instance, the atomic volume of potassium is 45.2, and the molecular volume of KCl is 37.4. The compound occupies less space than one of its constituents. Kopp endeavored to derive a set of values for atomic volumes of the elements from the molecular volumes of their compounds, such that the latter might in turn be calculated as the sum of the former, as he did for liquids. The atomic volume proved to be dependent upon the nature of the compound, upon the position of the atom in the molecule, as we may imagine it, a constitutive property in short. No useful regularities have as yet been established, but there is value in the idea.

It is worthy of note that comparing the molecular volumes of closely analogous compounds the same differences are observed. This is shown in the following table of molecular volumes:

KCl..... 37.4	NaCl..... 27.1	AgCl..... 25.6
KBr..... 44.3	NaBr..... 33.8	AgBr..... 31.8
KI..... 54.0	NaI..... 43.5	AgI..... 42.0

Chlorine is most active, and iodine least active, chemically, and the chloride of any one metal occupies a smaller volume than the bromide, and the iodide occupies the largest volume. Whether such contractions will ever be interpreted as numerical measures of chemical energy cannot be predicted.

The Covolume of Solids. The covolume of solids does not seem to be a constant value. If it were we should have what we very much want, a good method for determining molecular weights of solids.

* Molecular volume is the volume occupied by a molecular weight in grams, or the molecular weight divided by the specific gravity.

CHAPTER XVI

SOLUTIONS — I

OSMOTIC PHENOMENA AND THE THEORY OF DISSOCIATION IN SOLUTION

IN Chapter III we defined the terms solvent and solute, and defined a solution as a mixture chemically and physically homogeneous throughout, the proportions of which may be altered gradually without causing an abrupt change in any of its properties. The main difference then between solutions and chemical compounds is that the laws of constant proportions by weight do not apply to the former.

Classification of Solutions. It is customary to classify solutions according to the conditions of aggregation of their components, and in this way the following subheads are established: solutions of (*a*) gases in gases, (*b*) gases in liquids, (*c*) gases in solids, (*d*) liquids in liquids, (*e*) solids in liquids, (*f*) liquids in solids, (*g*) solids in solids. But all the advantages obtainable from a systematic treatment are retained if we adopt a less elaborate subdivision, based on the condition of aggregation of the solution, and consider: (*a*) gaseous solutions, (*b*) liquid solutions, (*c*) solid solutions.

Gaseous Solutions. Gases which do not interact chemically are miscible in all proportions, and these mixtures conform to the definition. Our most important generalization about gaseous solutions is both simple and comprehensive. When we have a gaseous mixture (gaseous solution), each gas exerts the pressure it would exert if it alone were present in that volume. This pressure is called the partial pressure of that gas and the total pressure of the mixture (solution) is the sum of the partial pressures. For instance, air is a solution, being a homogeneous mixture of oxygen and nitrogen and some other gases. The partial pressure of the nitrogen is about four-fifths of the barometric pressure, the partial pressure of the oxygen is about one-fifth of the barometric pressure, and the total pressure of the gaseous solution is the sum of these partial pressures.

All the properties of a gaseous solution are additive, the sum of the properties of the components. For instance, the properties of a given volume of air at a pressure of 760 mm. are the properties of that whole volume of oxygen at a pressure of 152 mm. plus the properties of that same whole volume of nitrogen at a pressure of 608 mm. (Of course this statement is not numerically exact, for it neglects the small partial pressures of other components as A, CO_2, etc., always present.)

Diffusion. As was brought out in connection with the kinetic theory, gases diffuse into each other almost independently of the attraction of gravitation. For instance, if we liberate some bromine at the bottom of a cylindrical jar full of hydrogen, the bromine will diffuse upward rather rapidly, and the progress of this diffusion is visible owing to the color of the bromine. Diffusion of one gas into another will not cease until the mixture is homogeneous throughout. This property of gaseous solutions is of vital importance, for it maintains the uniformity of composition of the atmosphere all over the earth. If it were otherwise, carbon dioxide, being heavier, would collect in a layer at the bottom and the earth would be uninhabitable.

Liquid Solutions. The properties of liquid solutions cannot be disposed of so summarily. Laws have been discovered to hold for dilute liquid solutions which have had great influence upon all branches of chemistry and also upon botany, zoölogy, and medical sciences. They require our careful consideration and we shall devote the rest of this chapter to them.

Such generalizations as we have regarding solid solutions will be made the subject of another chapter. Curious quasi-solutions are known, occupying, apparently, an intermediate position between true solutions and mechanical suspensions. We call these colloidal solutions. These too, in the light of recent work, have become of sufficient importance to be considered in a special chapter.

Dilute Solutions. By dilute solutions, as the term is understood in physical chemistry, we mean solutions of concentrations certainly not greater than one-tenth normal.*

* It may fairly be assumed that students have learned in previous courses the exact significance of these terms. We must use them freely from now on and to avoid any possible misunderstanding the following definitions are given. By concentration we mean the quantity of substance, expressed in any convenient units, present in unit volume, and entirely disregarding whatever else may or may not be present simultaneously in the same volume. By molecular normal solution we mean a solution of such concentration that a molecular weight in

Diffusion of Solutes. If we place a layer of water carefully over a sugar solution in such a way that the two do not mix, the sugar will rise slowly against the attraction of gravitation, until the whole solution is homogeneous. If we use copper sulphate instead of sugar, it is possible to follow the process by the color change. This is analogous to the diffusion of a heavy gas upward through a lighter gas, or analogous to the filling homogeneously and completely of the whole volume at its disposal by any gas.

There is then a force causing a solute to diffuse and it is probably of the same character as the force causing a gas to diffuse. We have no ultimate explanation for either phenomenon. We may adopt the kinetic theory and say the molecules are flying about with great velocities but the question remains unanswered, why do they so fly?

Semipermeable Membranes. We have found a number of membranes which, placed between a solution and the pure solvent, permit the passage of the latter but more or less completely prevent the passage of the solute. Such membranes are styled "semipermeable."

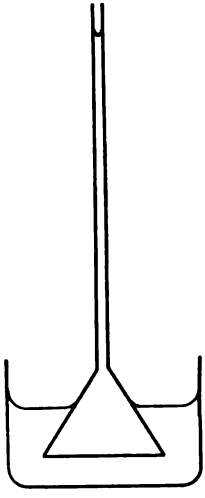


Fig. 25.

Qualitative Experiment. Tie parchment paper over a small glass funnel, make the joint tight with sealing wax, fill it with a concentrated solution of sugar, attach a long glass tube to the stem by rubber tubing, and invert in a beaker of distilled water, as shown in Fig. 25. Water passes through the parchment, and the volume of the solution being increased it rises in the tube. It is very easy to set up the apparatus in such a way that the meniscus in the tube rises several centimeters an hour and to a height of ten or twelve feet. More or less sugar may be found in the water outside. The hydrostatic pressure usually breaks the sealing-wax joint when this height is attained.

Osmosis. This development of an hydrostatic pressure on the solution side of such a membrane is called osmosis and the pressure so measured is called osmotic pressure.

grams of the solute is present in a liter of the solution. By equivalent normal solution we mean one of such concentration that an equivalent weight in grams of solute is present in a liter of the solution. The term "normal solution," without qualifying adjective, in this book, is used to indicate molecular normal. If equivalent normal is intended the term equivalent normal will be used.

Endosmosis and Exosmosis. Abbé Nollet (1700–1770) in 1748* filled a vessel with alcohol, closed it with bladder, submerged the whole in water, and observed that the volume of alcohol was increased and the bladder distended. These facts were forgotten and the phenomenon was rediscovered by Sömmering in 1814. It was first seriously studied by Dutrochet, and by N. W. Fischer, in numerous articles beginning in 1822. The underlying idea of many suggestions which have since been made as plausible explanations may be found in one or another part of Dutrochet's writings. He it was who gave us our nomenclature. Observing that there was always a current inward, to the side where the excess pressure developed, and a current outward, through such membranes, he called the first the endosmotic, the second the exosmotic current. For many years the phenomenon was called endosmosis and only relatively recently has it been abbreviated to osmosis.

Other Membranes. Many other diaphragms were found by the early investigators which gave the same qualitative results; for instance collodion, thin plates of marble, fine-grained unglazed porcelain, even glass with exceedingly fine cracks in it such as may be produced by bringing water in contact with a hot test tube, almost any animal membrane, as the lining of the peritoneal cavity, or the heart sack, have been used. Plant cells are enclosed sacks with this property of permitting the passage of a solvent while hindering more or less perfectly the passage of dissolved substances.

Evidently some of the most important processes of both animal and vegetable life are thus osmotic, and consequently the phenomenon is of great general interest.

Ideal Membranes. With all the efforts which have been expended we have not as yet found a perfect semipermeable membrane, one which offers free passage to the solvent while absolutely preventing the passage of all traces of the solute. The nearest approach to a realization of the ideal membrane was made by M. Traube,† who discovered the so-called precipitation membranes of which copper ferrocyanide is the best example.

Copper Ferrocyanide. Fill a beaker or jar with a solution of copper sulphate. Make a solution of potassium ferrocyanide of slightly greater specific gravity. Fill a pipette with this, put the opening of the pipette below the surface of the copper sulphate solu-

* "Memoires de l'Academie Royale des Sciences" (1748), pp. 57–104.

† *Archiv für Anatomie und Physiologie* (1867), p. 87.

tion and let a little of the potassium ferrocyanide solution flow out slowly. Where the two solutions come in contact a precipitate of copper ferrocyanide forms as an exceedingly tenuous membrane, effectually separating the two solutions. Where it breaks it repairs itself, new membrane forming. That the solutes cannot pass through is demonstrated by the fact that the membrane thickens only very slowly. That water passes readily is proved by the fact that a more concentrated solution of copper sulphate collects all about the bubble and may be seen falling in threadlike streams from the lowest points. If the bubble is shaken loose from the pipette it will sink, owing to its greater specific gravity, but the potassium ferrocyanide solution inside is constantly gaining water at the expense of the copper sulphate solution, and eventually the specific gravities are reversed and the bubble slowly ascends through the liquid to the surface. This is a particularly significant experiment, easily carried out, and we shall have occasion to refer to it again.

Maximum Osmotic Pressure. The question arises, what is the maximum osmotic pressure obtainable with a given solution? To determine this we must have as nearly ideal a semipermeable membrane as possible, and it must withstand the pressure without breaking. The copper ferrocyanide membrane comes nearer to fulfilling the first requirement than any other we have yet discovered, but it is very fragile.

The botanist W. Pfeffer* had the ingenious idea of precipitating copper ferrocyanide within the pores of unglazed porcelain cells, thus furnishing strong supports for exceedingly small areas of membranes. He placed a solution of potassium ferrocyanide inside such a cell and an equimolecular solution of copper sulphate outside, and allowed time for these substances to diffuse and meet in the pores. Several days are required and about nineteen out of twenty of the membranes so formed are defective. But he secured a number with which he made the first quantitative measurements of maximum osmotic pressure. In his best cells the membranes were, as you might say, plastered on the interior surface rather than actually within the body of the porcelain.

Pfeffer's Apparatus. A somewhat simplified form of his apparatus is shown in Fig. 26. The small cylindrical porous cup carrying the membrane is cemented tightly to the glass part. A closed mercury manometer is used in order to measure high pressures and

* "Osmotische Untersuchungen," by W. Pfeffer, 236 pp. (1877).

yet hold the volume increase as low as possible. The cell is filled completely with solution of known concentration through the tube *A*. This tube is then sealed and the whole arrangement is submerged in distilled water at a definite, constant temperature. The pressure within gradually rises, and in a day or more it reaches a maximum. Pfeffer discovered that his maxima were directly proportional to the concentrations of his solutions.

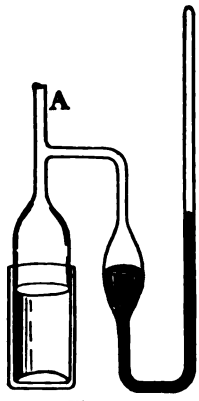


Fig. 26.

Plasmolysis. He also did much work with small plant cells. These consist of cellulose walls lined with membranes of protoplasm, which in turn enclose solutions. They are so small they must be studied under a microscope. Such a cell may be immersed in a solution, and if water enters the cell will swell until it bursts. If water leaves the interior the cell will shrink, the membrane of protoplasm will be separated from the inside of the cellulose wall, and we have the phenomenon called plasmolysis.

Isotonic Solutions. The concentration of the outer solution may be altered until no change of size is observed. When this condition is reached, the solutions inside and outside may be considered as exerting the same osmotic pressures. Such solutions are called isotonic or isosmotic. If such a cell does not alter upon being transferred from a solution (*a*) to a solution (*b*), then (*a*) and (*b*), each equal to a third, must be equal to each other, and they too are isotonic.

Temperature Effect. Pfeffer also observed that when a cell shows no change in a given solution, the temperature of cell and solution may be altered and still there will be no change in its size. This proves the osmotic pressures of different solutions change at the same rate with changes of temperature.

Van't Hoff's Generalization. In 1886 J. H. van't Hoff calculated from Pfeffer's results that the maximum osmotic pressure obtainable with a solution of a given concentration is the same as the gaseous pressure which that much of the solute would exert if we could have it as a gas in that volume at that temperature. For instance, the maximum osmotic pressure obtainable at 0° with a solution of sugar of such a concentration that 22.4 liters contain a molecular weight in grams, is 760 mm. of mercury, or one atmosphere. A normal solution of sugar contains a molecular weight in grams in

one liter, and the maximum osmotic pressure obtainable with it is 22.4 atmospheres.

In other words, Boyle's law holds for substances in solution without alteration of the numerical significance of any one of the symbols; we must only substitute the words " maximum osmotic pressure " for gaseous pressure.

Van't Hoff also calculated from Pfeffer's results that the maximum osmotic pressure for a given solution is directly proportional to the absolute temperature, that is, Gay-Lussac's law applies to substances in solution. Combining these facts, he said that the gas laws, as expressed in the fundamental equation $pv = RT$, apply to substances in solution without alteration of the numerical value of any one of the symbols. This is the greatest generalization ever made regarding solutions.

Experimental Verification. The experimental difficulties in making direct measurements of maximum osmotic pressures are enormous, and therefore, for years, the experimental basis for this great generalization was slender. But recently H. N. Morse in America and the Earl of Berkeley in England have made many improvements in the methods and many quantitative measurements.* One of the most useful of these improvements is in the method of making the membrane. Morse inserted electrodes in the solutions on opposite sides of the porcelain and, applying an electromotive force of about 100 volts, drove the membrane-forming constituents into the porcelain. This much shortens the time needed and diminishes the percentage of poor membranes. Such membranes have withstood pressures as high as 130 atmospheres and have proved to be nearly ideal as regards semipermeability.

Exceptions. Just as we have no ideal gas, so have we no ideal solution. Just as we found it necessary to apply corrections to the gas laws in order that they might more nearly formulate the actual

* For full experimental details and the best data we have at present the reader is referred to the following articles:

By H. N. Morse and coworkers, *Am. Chem. Jour.*, **26**, 80–86 (1901); **28**, 1–23 (1902); **29**, 173, 174 (1903); **34**, 1–99 (1905); **36**, 1–39, 39–93 (1906); **37**, 324–360, 425–467, 558–595 (1907); **38**, 175–226 (1907); **39**, 667–680 (1908); **40**, 1–18, 194–213, 266–277, 325–337 (1908); **41**, 1–19, 92–117, 257–276 (1909).

By Earl Berkeley and E. G. J. Hartley, *Proc. Roy. Soc.*, London, **73**, 436–443 (1904); **77**, 156–169 (1906); *Phil. Trans. Roy. Soc.*, London, **206**, 481–507 (1906); *Proc. Roy. Soc.*, London, **82**, 271–276 (1909); *Phil. Trans. Roy. Soc.*, London, **209**, 177–203 (1908); 319–336 (1909).

behavior, and introduced van der Waals' corrections, so must we apply corrections in order that they may formulate the behavior of solutions. We subtracted the constant b, supposed to be four times the volume actually occupied by the molecules, from the measured volume of gases. The work of Morse and Berkeley shows that if we subtract the volume occupied by the solute from the total volume of the solution, the experimental values for maximum osmotic pressures are much nearer those calculated according to the gas laws. The exceptions themselves thus strengthen and confirm the remarkably close analogy between the gaseous condition of aggregation and the condition of being in solution.

Colligative Properties. A property, numerically the same for a group of substances, independent of their chemical natures, Ostwald has called colligative. The gaseous pressure is independent of the nature of the gas and hence a typical colligative property. The maximum osmotic pressure of a substance in solution had been proved to be independent of its chemical nature and is therefore another colligative property. Whenever we find a colligative property we may use it to determine molecular weights. Therefore we may determine molecular weights of substances in solution by determining their maximum osmotic pressures.

Molecular Weights. The reasoning is exceedingly simple. Our definition of a molecular weight is the weight in grams of a gas which, occupying 22.4 liters at 0°, exerts a pressure of 1 atmosphere. Since the gas laws apply without great corrections to substances in dilute solution we may apply the same definition. Suppose we find that a solution containing 10 grams of a substance per liter exerts a maximum osmotic pressure of 1 atmosphere. Then 22.4 liters of it will contain a molecular weight and the molecular weight is 10×22.4 or 224.

Suppose a solution contains 0.54 gram substance per 100 cm^3 and is found to exert a maximum osmotic pressure of 1.5 atmospheres at 0°. We have only to calculate the number of grams which must be present in 22 400 cm^3 to exert a maximum osmotic pressure of one atmosphere. We have $\frac{0.54}{100} \times 22\,400 \times \frac{1}{1.5} = 80.64$, which is then the molecular weight.

Indirect Measures. This application of the fundamental principles by which we determine molecular weights of gases to dissolved substances is important. There are many substances which do not lend themselves to measurement by the vapor density methods, but

almost everything will dissolve in some solvent and we may apply the osmotic method. Unfortunately direct measurements of maximum osmotic pressures are so difficult we cannot use them, but must have recourse to the so-called indirect methods. It will be explained in Chapter XXIII, how van't Hoff showed that the lowering of the freezing point and raising of the boiling point, due to the presence of a dissolved substance, is a measure of the osmotic pressure. Results by these methods are very numerous, and are being added to constantly. The indirect evidence of the validity of van't Hoff's great generalization, that the gas laws apply to substances in solution, is overwhelming.

Diffusion as a Method of Measurement. If the force causing diffusion of a dissolved substance through a solution is not identical with that causing the phenomena of osmosis, it is certainly very closely allied to it. Then measurement of the velocity of diffusion in liquids should be a measure of maximum osmotic pressures and so of molecular weights. We learned in Chapter XI that we can determine the molecular weight of a gas by measuring the rate at which it escapes through a capillary opening by applying the formula derived from the kinetic theory, $\frac{m_1}{m_2} = \frac{c_2^2}{c_1^2}$. Since the gas laws apply to solutions we should be able to determine the molecular weight of a dissolved substance by measuring the rate at which it diffuses. But the diffusion of a dissolved substance is a very slow process. A saturated solution of copper sulphate will not diffuse upward 20 cm. in a month sufficiently to give a marked blue color, at that level, if all mechanical shaking and temperature changes which might set up convection currents are eliminated.

Diffusion through Jellies. It has been found that crystalline substances diffuse through a jelly made with gelatine at the same rate as through pure water, provided the percentage of gelatine is not too great, say 4 to 5 per cent as a maximum. A tube is filled with gelatine jelly and a solution is caused to flow slowly by in contact with one face, while the other face is in contact with a slow current of distilled water. In this way the concentration is held nearly constant at each surface and the quantity of solute diffusing through in unit time is measured. The rate of diffusion is slow, for instance, 0.312 gram sugar from a 1 per cent solution passed through one square centimeter of a gelatine membrane 1 centimeter thick in 24 hours. Because of its slowness diffusion is not a practical method for determining molecular weights.

Osmotic Pressures in Other Solvents than Water. Thus far we have no quantitative direct measurements of the maximum osmotic pressures of substances in other solvents than water. This is due to the fact that we have not as yet found membranes conforming sufficiently well to the requirement of almost perfect semipermeability, that is, permitting the passage of the solvent and preventing the passage of the dissolved substance, for any other solvent than water.

Attempts to Explain. We have now before us the typical facts regarding osmosis. In spite of many efforts a wholly adequate, plausible explanation for them is still lacking. The suggestions which have been made are legion, and it is entirely out of the question to discuss them all. Omitting minor variations, they may be grouped under three heads: the kinetic hypothesis, the attraction hypothesis, and the surface tension hypothesis.

The Kinetic Hypothesis. The fact that the gas laws apply to substances in solution suggests at once that osmotic pressure is due to the same cause to which we attributed gaseous pressures, namely, a bombardment of the membrane by the dissolved molecules.

Arguments in Favor of the Kinetic Hypothesis. The main arguments in favor of this hypothesis are of course the numerical equality of osmotic and gaseous pressures and the numerical identity of the temperature coefficients; in short, that the gas laws apply to substances in dilute solution.

Furthermore it must be conceded that it is the dissolved substance which in some way causes the exertion of the pressure, for, first, if no dissolved substance is present, no osmotic pressure is observable, and second, it would be absurd to attribute the pressure to the solvent, for the membrane is obviously permeable to the solvent, and we might as well imagine a column of water resting on a sieve as a base as that the solvent exerts these high pressures on the membrane and yet does not go through.

Van't Hoff has suggested an experiment which illustrates how we may apply the kinetic theory to solutions. Suppose a mixture of nitrogen and hydrogen confined in a palladium vessel which is immersed in an atmosphere of hydrogen. Palladium, especially at high temperatures, as is well known, is readily permeated by hydrogen but not by nitrogen. The pressure within this vessel is a gaseous pressure, the sum of the partial pressures of the hydrogen and the nitrogen. Now suppose that we lower the temperature and increase the pressure on the whole system until these gases liquefy. The

excess pressure within the vessel at any time during this process is evidently due to the nitrogen, and is a gaseous pressure. When liquefaction is complete, the excess pressure in the vessel is still due to the nitrogen, although this is now a liquid, and is dissolved in the liquid hydrogen just as sugar is dissolved in water.

Perrin has shown (see Chapter XI) that the Brownian movement of the smallest particles observable by ultramicroscopic methods is of the order calculable from the kinetic theory. It is reasonable to extend this conclusion to yet smaller particles such as we imagine the particles of a solute to be.

Arguments against the Kinetic Hypothesis. The solvent passes through the membrane to the solution. By no stretch of the imagination can one conceive of a vigorous bombardment on one side of a membrane as determining a flow of water in a direction opposed to such bombardment.

Liberate a gas in a vessel and all parts of the vessel feel the full force of the pressure immediately. Osmotic pressures grow gradually and require some little time to reach their maxima. This is not an important objection. The full force may indeed be there at the outset, for our methods of measurement would not detect it. The force must do work to affect a manometer, and that takes time, but the force itself may be the same when the process starts as when equilibrium is reached.

Such great pressures should crush any vessel immersed in a solution. This contention is untenable, for the vessel, unless semipermeable, is not subjected to the pressure. There is a liquid surface surrounding it and the intermolecular attractions in operation forming a surface are directed inward, and so are opposed to osmotic pressure. They are probably far greater than osmotic pressures, large as the latter are.

It is difficult to imagine dissolved molecules moving with the velocity of gaseous molecules because of the great internal friction of liquids shown by the slowness of diffusion in them. This objection finds an experimental answer in the work of Perrin already cited.

The Attraction Hypothesis. In the attraction hypothesis, the assumption is made that the solvent passes through to the solution because of the affinity, probably chemical, of the solute for the solvent. This has been cleverly dubbed the "thirst" hypothesis, and it has been suggested that we should speak of "osmotic suction" rather than "osmotic pressure."

Argument for the Attraction Hypothesis. Chemical affinity is almost the only force we can think of, if we exclude gaseous pressures, adequate to produce the large pressures actually observed.

Arguments against the Attraction Hypothesis. The great difficulty with this hypothesis is that it does not account for van't Hoff's generalization. We cannot imagine that the chemical affinity between water and equimolecular quantities of all substances whatsoever is exactly the same. Nor can we readily accept a statement that this attraction between all solutes and water increases in direct proportion to the absolute temperature. On the contrary we should expect that the " thirst " of many substances would diminish as the temperature increased, for substances lose water of crystallization at relatively low temperatures.

If the driving force be an attraction, it should diminish as the square of the dilution increases. As a matter of fact, it falls off directly as the dilution increases.

Surface Tension Hypothesis. We may consider the solution and the pure solvent as contained in two elastic bags and the surface tensions are the measures of the forces striving to diminish the external areas of the bags. That bag with the greater surface tension will squeeze its contents into the other.

In many cases the facts are in accord with this hypothesis and the motion of the liquid through the membrane is from the side of greater surface tension to that of less.

But many other cases are known wherein the motion is the other way, from the side of less surface tension to that of greater. Under these circumstances we cannot concede much value to this hypothesis in its simple form as just described. It has been bolstered with additional hypotheses, some of them rather forced, until it has become so complicated that it is certainly not illuminating as a really good and useful hypothesis should be.

Conclusion. Considering all the suggestions made, we recognize good and bad in each, which means that each doubtless contains value, and that some day we may devise a composite which will be better than any one alone. Apparently there is more of value in the kinetic hypothesis than in the others. But for the present at least we are forced to the conclusion that we have no really satisfactory plausible explanation of the facts of osmosis. There is no reason why this should excite surprise or any unusual amount of dissatisfaction, for we have no satisfactory explanation for the commonest, simplest

event. That it does excite dissatisfaction is undeniable and this is an indication that we overestimate our achievement when we have devised a satisfactory theory such as the kinetic theory of gases or Avogadro's theory or the like.

The Function of the Membrane. By some, the function of the membrane in osmotic phenomena is considered to be a subordinate question, because it can be demonstrated that the nature of the membrane, assuming perfect semipermeability, makes no difference. This demonstration runs as follows: Imagine a long tube divided into compartments by two diaphragms, perfectly semipermeable, but of such natures that the first is capable of " generating " a higher osmotic pressure than the second. Imagine the chamber made by the diaphragms filled with a solution and the rest of the tube full of water. Water will pass in through both membranes until the pressure is the maximum the second can generate. It will continue to come in through the first but will then begin to pass out through the second. Since the membranes are not altered, and all solute is retained in the chamber, water will continue to flow in through the first and out through the second forever. We could insert a water wheel and make the current do work, thus realizing a perpetual motion machine, one to do work at no expense. Such a machine is impossible, therefore the two diaphragms cannot have the difference assumed for them. Therefore the maximum osmotic pressure must be the same for all perfect membranes. This is entirely conclusive, being just as certain as the premise that a perpetual motion machine is impossible, but like so much thermodynamic reasoning it leaves us exactly where we started without adding one iota to the actual sum of our knowledge.

As a matter of fact we seldom have to do with conditions wherein even approximately maximum osmotic pressures become evident, but we have to do constantly, whether we will or not, with what we may call traces of osmotic pressures, for the majority of our life processes are secretions by glands, and through membranes which permit the passage of this and hinder the passage of that. Unless the countless membranes in our bodies have their appropriate permeabilities, sickness and death ensue. Hence the majority are not satisfied to let the matter rest with a thermodynamic demonstration that the nature of the membrane makes no difference but will continue experimental investigations in the hope to find a cure for indigestion, rheumatism, and allied complaints.

Capillary Structure. The earliest publications on osmosis considered the membranes as capillary structures, and many were the efforts to account for the endosmotic and exosmotic currents on the basis of the behavior of liquids in capillary tubes. One liquid adhering closely to the inner walls constituted a liquid tube moving in one direction while an interior core of the other moved in the opposite direction. These suggestions are not satisfactory as a statement of the cause of the observed effects.

Sieve Effect. Then it was thought these capillary structures acted like sieves, permitting the passage of molecules of solvent because they were smaller than the holes, and preventing the passage of solute because its molecules were larger than the holes. It has been brought forward against this theory that membranes are known which permit the passage of the large molecules of various alkaloids while holding back the smaller molecules of amido acids. It is here silently assumed that the size of the formula we write for a substance is a measure of the size of the individual molecule. This is rather hypothetical. The argument might be met on its own ground by the assumption that a very long carbon chain might worm its way through a hole so small a benzene ring could not enter.*

Membranes as Solvents. Experiments of extraordinary interest were carried out by Lhermite.† In a test tube he put some water, above this a thin layer of castor oil, above this a layer of alcohol. In the course of a day or two the alcohol had passed through the oil to the water and there were but two layers in the tube, the solution of alcohol in water and the oil above it. He substituted turpentine for the oil with the same result. He separated a layer of chloroform from a layer of ethyl ether by a layer of water and the ether passed through to the chloroform. He tried eight different combinations. Of particular interest, as foreshadowing our present devices, is the following experiment of his: He put alcohol in a porous cup, immersed it in water and observed that the water passed in to the alcohol. He next filled the pores of the cup with castor oil, filled the cup with alcohol and immersed it in water as before. With this modification

* The writer in conjunction with F. E. Bartell has estimated the size of the capillary holes in the coarsest-grained porcelain with which small, but definite osmotic pressures may be obtained, and finds the diameters of these holes in the neighborhood of one thousand times the probable diameters of molecules. For details, see *Jour. Am. Chem. Soc.*, 31, 1194–1199 (1909).

† *Ann. de Chim. et de Phys.* (3) 43, 420–431 (1855).

the alcohol passed outward to the water. As a result of these experiments he stated that substances which pass through membranes first dissolve in them. Many investigators at present entertain the opinion that membranes with which osmotic phenomena may be produced must be able to dissolve the substance which passes through. That this is not essential is proved by the fact that small excess pressures may be obtained with a cracked test tube for a membrane.

It is possible to look upon a liquid, or solution, as a capillary structure, for there must be space between the molecules else it would be continuous, infinitely divisible, and we should have to abandon our molecular theory.

Very much more might, and possibly should, be said in connection with this interesting topic of osmotic pressures, but space will not permit. We must conclude with the statement that, while we know many interesting facts, we have not at present an entirely satisfactory theory to account for the phenomena nor even for the way the membrane acts.*

Abnormal Osmotic Pressures. Many substances in water solution show greater osmotic pressures than we should expect. By means of plant cells or any other method of direct comparison, we may prepare isotonic solutions of sugar and of potassium chloride. If we determine the concentrations of the dissolved substances in these solutions in terms of molecular weights in grams per liter, we shall find that the concentration of the sugar solution is almost double that of the potassium chloride solution.

The Isotonic Coefficient. Van't Hoff observed this variation and expressed it in terms of what he called the isotonic coefficient, which he denoted by i. This i represents the ratio between the observed "abnormal" maximum osmotic pressure of one solution and the maximum osmotic pressure of an equimolecular solution which gives "normal" osmotic pressures. For instance, if we have equimolecular solutions of calcium chloride and of sugar, the maximum osmotic pressure found for the calcium chloride solution divided by the maximum osmotic pressure found for the sugar solution gives

* The literature of the subject is extensive. The reader is referred for additional information to "Osmotische Druck und Ionenlehre in den Medicinischen Wissenschaften," by H. J. Hamburger, 3 volumes. Vol. I, 539 pp. (1902); Vol. II, 516 pp. (1904); and Vol. III, 508 pp. (1904). "Physikalische Chemie der Zelle und der Gewebe," by R. Höber, 344 pp. (1902). "Du Rôle Chimique de la Membrane dans les Phénomènes Osmotique," by G. Flusin (1907). These works contain many references.

us the value *i*, the isotonic coefficient. When the solutions are dilute, let us say one-thousandth normal, calcium chloride gives about three times as large an osmotic pressure as an equimolecular solution of sugar, and thus the isotonic coefficient is nearly three.

The Behavior of Potassium Ferrocyanide Bubbles. Suppose that we prepare normal solutions of copper sulphate and potassium ferrocyanide. The molecular weight of copper sulphate is 159.6, that of potassium ferrocyanide is 368.6. Disregarding the change in volume which occurs upon solution, for this change is small, a liter of the potassium ferrocyanide solution weighs 209 grams more than a liter of the copper sulphate solution, and therefore is specifically heavier. In the experiment described earlier in this chapter, the potassium ferrocyanide bubble sinks in the copper sulphate solution.

These solutions being equimolecular should be isotonic, but they are not. Water passes from the copper sulphate solution through the membrane increasing the internal volume, diminishing the concentration, diminishing the specific gravity, until the potassium ferrocyanide bubble rises.

Water solutions of all acids, bases and salts were found to give abnormal, too great, osmotic pressures and apparently could not be included in van't Hoff's generalization.

Electrolytic Dissociation Theory. In 1887 S. Arrhenius (1859–) published his theory of electrolytic dissociation of dissolved substances, based on facts of electrochemistry, and as a plausible explanation of these osmotic phenomena, just before van't Hoff arrived at the same conclusions.*

Apparently too many Molecules. These abnormal osmotic pressures are exceptional, all of them, in the sense that with a given volume and temperature the pressures are too great. If Avogadro's theory be applied, we have, apparently, too many molecules. Of course we might say that Avogadro's theory does not apply, but for many cogent reasons we choose to consider that it does, and that we have too many molecules.

Deviations Reach a Maximum upon Dilution. In dilute solutions the exceptions are more marked than in concentrated solutions, and by increasing the dilution we are able to reach a condition where a dissolved substance shows a behavior characteristic of the presence of almost twice as many, or almost three, or some other

* *Zeitschr. f. phys. Chem.*, 1, 631–648 (1887).

small whole number of times as many molecules as we calculate to be present. When this value has been reached, further dilution does not continue to increase the effect. It has reached a maximum.

Analogy with Gaseous Dissociation. All of this is strikingly analogous to the phenomena which we discussed under the title of "abnormal vapor densities." We found these "abnormalities" were due to dissociation of the gaseous molecules.

Dissociation into Ions. In the same way, we are able to account plausibly for these abnormal osmotic pressure results by assuming that those substances which show them, on going into solution, dissociate more or less completely into two or more parts. Following the terminology introduced by Faraday we call these parts ions.

Electrolytes. Substances giving normal osmotic pressures do not conduct electricity in water solution, while substances giving abnormal osmotic pressures do. These latter are called electrolytes and include acids, bases and salts.

The facts of electrochemistry are needed to enable us to decide where the break, or breaks, occur when a molecule dissociates. We assume the parts are electrically charged and that each molecule gives one or more ions charged plus, called cations, and one or more charged minus, called anions. The sum of the plus charges on the cations resulting from the dissociation of one molecule must equal the sum of the minus charges on the anions from the same molecule.

We have learned that the cations must be considered as comprising hydrogen and the metals and the anions as comprising the hydroxyl group and the acid radicals.

Number of Charges. These ions have capacities for chemical combination, that is valence, and to each unit capacity for chemical combination there corresponds the definite quantity, 96 500 coulombs of electricity (see Chapter XXVIII). We therefore call this "unit quantity of electricity" and say that every univalent ion (by which we mean a gram formula weight of it) is charged with unit quantity of electricity; a bivalent ion with two unit quantities of electricity, and so on.

Electrons. If we choose to adopt the granular, or atomic, theory of electricity, instead of the older conventions of plus and minus, we may consider a univalent anion as whatever its formula stands for plus one electron, a bivalent anion as plus two electrons and so on. We must then consider a univalent cation as whatever its formula stands for minus an electron, etc.

Indicating Ions. We indicate that a substance is present as a cation by adding a dot for each unit charge, or valence, or electron, at the upper right-hand corner of the symbol as follows: $K^{\cdot}$, $Ca^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, and that it is present as an anion by adding an apostrophe for each charge, or valence, or electron, in the same position. For example, Cl', SO_4'', PO_4'''.

Similarity between Ions and Molecules. These ions seem to have the value and properties of molecules in solution. We consider them as leading independent existences except that they must attract each other owing to their heavy opposite charges. In any solution, for every unit of positive electricity there must be a unit of negative electricity, and we cannot remove plus charges from cations without simultaneously removing the same number of minus charges from anions.

Ions resemble molecules more than atoms, but cannot be supposed to be identical with either because of the electrical charges. It would, of course, be absurd to think of a metal such as sodium existing in contact with water, for we know well that this substance decomposes water vigorously with the evolution of hydrogen. But an atom of sodium carrying a unit of positive electricity is something wholly different from the metal itself. The addition of this electricity changes its properties fundamentally, and it is justifiable to consider sodium ions in solution as an allotropic modification of the element. The differences in properties of metallic sodium and sodium ions are not greater than the differences between the allotropic modifications of phosphorus or carbon.

Ionized substances should be considered as definite forms of matter. We therefore speak of hydrogen ion or sodium ion, of sulphate ion or chloride ion, as we speak of any substance, different from other substances, with properties of its own.

Explanation of Abnormal Osmotic Pressure. The explanation of abnormal osmotic pressures by means of the electrolytic dissociation theory is immediate and logical. The molecules of potassium chloride for example are supposed to dissociate to a considerable extent into the cation $K^{\cdot}$ and the anion Cl' in concentrated solutions. As we dilute, this dissociation increases until it is practically complete in $\frac{n}{1000}$ solution. Each ion having the properties of an independent molecule we obtain an osmotic pressure more and more abnormal as we dilute until at last, with complete dissociation, we obtain a maxi-

mum osmotic pressure which is twice what it would be were there no dissociation. Thus $\frac{n}{1000}$ KCl completely dissociated is isotonic with $\frac{n}{500}$ sugar, which does not dissociate. Calcium chloride dissociates according to the scheme, $CaCl_2 = Ca^{\cdot\cdot} + 2\,Cl'$, and so one molecule gives three ions, each having as much osmotic effect as a molecule. Thus, $\frac{n}{1000}$ $CaCl_2$, if completely dissociated, is isotonic with $\frac{n}{333.3}$ sugar.

Application to the Potassium Ferrocyanide Bubble. Copper sulphate gives us the two ions $Cu^{\cdot\cdot}$ and SO_4''. Then $\frac{159.6}{2}$ or 79.8 is what we might call the average molecular weight of the substance in dilute solution. Potassium ferrocyanide gives us five ions, four $K^{\cdot}$ and one $Fe(CN)_6''''$. Then $\frac{368.6}{5}$ or 73.7 is what we might call the average molecular weight of this substance in dilute solution.

Then solutions containing 79.8 grams of completely dissociated copper sulphate and 73.7 grams of completely dissociated potassium ferrocyanide should be isotonic. Disregarding the small change of volume upon solution we see from these figures that a liter of the potassium ferrocyanide solution containing 73.7 grams must be 6.1 grams lighter than a liter of copper sulphate solution containing 79.8 grams, and therefore the potassium ferrocyanide must rise. The solvent does pass through the membrane into the potassium ferrocyanide solution until the latter becomes specifically lighter and rises. This is striking experimental evidence of the high degree of probability of our reasoning. Abnormal osmotic pressures are but one group of many and widely different phenomena which we can explain by means of the dissociation theory, and for which we have no other so satisfactory an explanation.

The theory of electrolytic dissociation has furnished a logical explanation for many facts throughout all branches of chemistry, which, before its advent, were without plausible explanation. It has proved its usefulness as a premise from which new facts have been deduced and it has been a reliable guide for research in many cases. Therefore it must be considered as on a par with the atomic and molecular theories. Perhaps all three theories are correct statements of facts if we only knew it; perhaps they are all wrong. We do not know be-

cause they are all theories. It is difficult to understand how anyone can accept and use one or two of these theories and reject or refuse to use the other or others. Yet such individuals may be found.

It is not necessary to say more regarding the theory at present for two reasons: first, it is doubtless familiar from previous study, and second, it will be used time and time again in the rest of this book as the most plausible explanation of facts, in the same way as the atomic and molecular theories.

CHAPTER XVII

SOLUTIONS — II

ROTATION OF THE PLANE OF POLARIZED LIGHT

IN Chapter XV we discussed at some length what we mean by plane polarized light, described the nicol prism and simple polariscope, and remarked that the most important applications of the latter, from the point of view of the chemist, is in the study of solutions. We shall now consider some of these applications.

Polariscope. A polariscope for use with solutions consists of a polarizing nicol and an analyzing nicol far enough apart to permit us to insert tubes containing the solutions. These tubes are either 10 cm. or 20 cm. long, and about 1 cm. in internal diameter. The ends are carefully ground so that when they are closed by plate glass disks held on by screw caps, these disks are parallel to each other. The whole tube fits in a metallic trough and light from the polarizer must then pass through the solution the length of the tube before reaching the analyzer. A metallic cover excludes light from the sides.

Some pure liquids and many solutions possess the power of rotating the plane in which polarized light is vibrating. If a tube filled with such a substance or solution be placed between the polarizer and analyzer, the analyzer must be turned through an angle in order that the polarized light whose plane has been rotated by the substance shall pass through undiminished; and it is evident that the angle through which the analyzer must be turned is a measure of the angle through which the plane of polarized light has been rotated by the substance. The analyzer is mounted in the center of a graduated metallic disk. The angle through which the disk is revolved is read by means of a vernier and lens fixed on the instrument.

Rotary Dispersion. Light of different wave lengths is rotated to different degrees producing the phenomenon known as rotary dispersion. To obviate the difficulties arising from this effect we use homogeneous light, light of a definite wave length, generally that of a sodium lamp, although particular lines of the spectra of certain elements are sometimes used.

Half-shadow Device. Looking through the instrument at the field of light, it is hard to determine in just what position it is brightest, and equally hard to determine in just what position we have total darkness. To obviate this difficulty we employ what is known as the half-shadow apparatus. Within the instrument, just behind the polarizer, is set a plate of quartz covering half the field of light. Quartz rotates the plane of polarized light, and thus we have, starting through the instrument, a field of polarized light, one-half of which is vibrating in a plane at a slight angle to that in which the other half is vibrating. In Fig. 27, diagram *a*, the shading may be

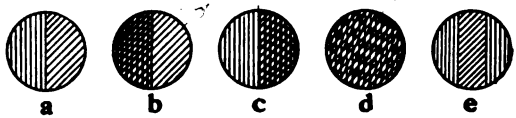


Fig. 27.

taken as representing the two planes in which the polarized light starts through the instrument.

Now if the analyzer, considered as a screen, is parallel to the vibrations in one-half of the field, this half will appear bright, while the other half will appear somewhat darker as shown in diagram *b*. If the analyzer be parallel to the vibrations in the other half, that will appear bright, and the first somewhat darker, as shown in diagram *c*. The only conditions under which the field will appear uniform is when the screening effect of the analyzer bisects the angle made by the two planes of vibration, as shown in diagram *d*. While it is difficult to determine maximum light or maximum darkness, it is not hard to match intensities of light in fields immediately bounding each other, and this ingenious device enables us to set the analyzer accurately.

In some polariscopes, instead of a plate covering half the field, a strip of quartz is inserted covering a band through the center. The principle is exactly the same, but in the judgment of many it is easier to match light intensities with this arrangement than with the other. The effect is adequately demonstrated in diagram *e*.

Using a polariscope, we first find the zero point, reading off the position on the graduated circle by means of the vernier and lens. We then insert the substance, rotate the analyzer until the fields once more match, and again read the angle. The difference in these two readings is the angle through which the plane has been rotated by the substance.

Solutions which Rotate the Plane. Sugar, tartaric acid and a large number of other substances in solution in water, and also in other solvents, rotate the plane of polarized light. We call them optically active. Almost all substances with this property are compounds containing carbon, but recently other compounds have been found possessing this same ability.

Rotating Power is a Constitutive Property. For any one substance the power of rotating the plane of polarized light is additive, for if we double the thickness of the layer between the two nicols, we double the angle through which the plane is rotated. But comparing different substances, we find it to be strictly a constitutive property, practically always coincident with the presence of a particular hypothetical grouping about one or more carbon atoms.

Effect of Temperature. An increase in temperature increases the rotation, and therefore we must hold the temperature constant during our observations, and since we have not as yet discovered any law formulating the connection between the change in rotation and the change in temperature, we adopt a standard temperature and measure substances at 20°. Good polariscopes are provided with jacketed tubes similar to Liebig condensers, by means of which the liquids under investigation may be surrounded by water and so brought to, and held at, the desired temperature.

Specific Rotation of Pure Liquids. Before comparisons can be instituted, units of measurement must be established. The specific rotation (an inappropriate term) of a pure liquid, denoted by $[\alpha]$, is $\frac{\alpha}{Ld}$, where α is the observed angle through which the analyzer was rotated, L is the length of the tube (thickness of the layer) in decimeters, and d is the density (specific gravity) of the liquid.

Specific Rotation of Solutions. We have adopted a somewhat different convention to express the specific rotation of solutions. Instead of the density, d, we insert the concentration, c, of the solute in any convenient units. As the values are usually small it is part of the convention to multiply the whole by 100. And so we have the formula for specific rotation of solutions, $[\alpha] = \frac{100\alpha}{Lc}$.

Moreover, as the rotating power differs with light of different wave lengths, the light to which the value is referred is also indicated in the formulation. If a sodium lamp be the source of light, this cor-

responds to Frauenhofer's *D* line, and this is indicated by *D* at the lower right-hand corner of the symbol for specific rotation. In order to give full information as to the conditions under which the measurement is made, we add also the temperature, putting it at the upper right-hand corner of the symbol, and thus get the expression $[\alpha]_D^{20^\circ} = \frac{100\,\alpha}{Lc}$.

Molecular Rotation. We have, in so many instances, discovered remarkable and valuable generalizations by merely converting the usual physical or metric units of expression into chemical units, calculating the quantity of the property pertaining to a molecular weight quantity in grams, that this has been tried for the property of rotating the plane of polarized light also.

Molecular rotation, as the name implies, is merely specific rotation multiplied by the molecular weight. It is commonly indicated by $[m]$, and inasmuch as these values are usually large, it is customary to divide by 100 and thus we get the formula for molecular rotation of pure liquids, $[m]_D^{20^\circ} = \frac{m\alpha}{100\,Ld}$.

Dextro- and Lævogyratory. Substances which rotate the plane in such a direction as to cause us to revolve the analyzing nicol in the same sense as the hands of a watch we call dextrorotary, or gyratory, and indicate this by the letter *d*, or by the sign +. Substances which cause us to rotate the analyzer in a direction opposed to that in which the hands of a watch move we call lævorotary, or gyratory, and we indicate this by the letter *l*, or by the sign −.

We have learned from experience that one and the same substance in different solvents has different rotary powers, but we have no explanation for this as yet.

Multirotation or Birotation. Freshly made solutions of some substances, for instance *l*-arabinose, *l*-xylose, *d*- and *l*-glucose, show definite rotating powers. But this rotation then alters continuously, in some cases growing larger, in others smaller, until it reaches a final value, usually after several hours. As we may thus read off a large number of values, the phenomenon is called multirotation.

As the initial rotation of a fresh solution of grape sugar is just double the final value, we sometimes call it birotation. We think the phenomenon is due to the existence of metastable forms which gradually change over to stable forms. The change is hastened by the presence of some catalytic agents.

Applications of the Polariscope. We depend on the polariscope almost entirely to identify and determine the purity or quantity of certain drugs. For instance, atropine and hyoscyamine are metamers with different physiological actions. The easiest way to determine the purity and quantity of atropine in a solution is by means of the polariscope.

Sugar Analysis. Polariscopes are in constant use to determine sugar quantitatively. This process is carried out so much that it has been reduced to a very simple routine, which is about as follows:

Weigh out 26 grams of the impure sugar and dissolve in enough water to make 100 cm^3 of solution. This solution is probably cloudy and dirty, containing suspended particles. Clear it by adding a little lead acetate or aluminium hydroxide, which causes these particles to collect and settle. Filter the solution and add distilled water until the volume is exactly 100 cm^3 once more. Put this into a tube exactly 20 cm. long, bring it to precisely 20°, and put it in a polariscope. Measure the angle through which the analyzer must be turned in order that the fields shall match. Refer to tables, which appear in every book on sugar analysis, giving the percentages of sugar corresponding to any angle which may be read.

Saccharimeters. Some polariscopes intended exclusively for use in sugar factories, or the custom house, are graduated, not in degrees and minutes, but in per cents of sugar, calculated on the assumption that these directions are carried out exactly. Such instruments are known as saccharimeters.

Wedge Instruments. We have instruments in which the analyzing nicol is not rotated, but compensation is produced by the in-

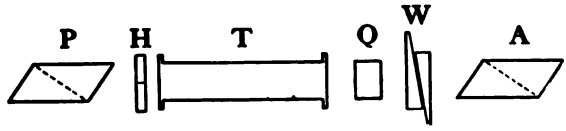


Fig. 28.

sertion of a quartz wedge. This arrangement was invented by Soleil, in 1848. A plate of quartz 1 mm. thick, cut perpendicularly to its optical axis rotates the plane of polarized sodium light $\pm$ 21.72° at 20°.

In the wedge instrument there comes first the polarizing nicol, *P* in Fig. 28, next the half shadow, or band-producing quartz plate, *H*, next the tube, *T*, containing the substance to be measured, next a

plate of left-rotating quartz, Q, next two wedges of right-rotating quartz, W, with their inclined surfaces close to each other but not touching. The larger wedge is carried by a micrometer screw and may be pushed in or pulled out. This double wedge thus provides that the surface at which the light enters is always parallel to the surface at which it emerges, and yet the thickness of quartz through which it must pass may be altered at will. After this comes the analyzing nicol, A, fixed in position. When the thickness of the combined wedges is equal to the thickness of the quartz plate, Q, these just compensate each other since they rotate the plane in opposite directions.

Suppose that in T we put a substance which rotates the plane to the left, then the right-rotating wedge must be pushed in further to compensate for this. If we put some right-rotating substance in T, then this wedge must be pulled out. It is easy to see how the distance through which the wedge must be moved, to compensate for the presence of the substance in T, may be utilized to determine the angle through which the substance has rotated the plane of polarized light.

Use of White Light. As a rule white light cannot be used with polariscopes because of rotary dispersion. But rotary dispersion produced by left-rotating quartz is rectified by right rotating quartz. It also so happens that the rotary dispersion produced by sugar solutions is the same as that produced by quartz. Therefore white light may be used with this wedge instrument in sugar analysis. It does not follow that other substances than sugar can be investigated with white light.

In General Concerning Optical Activity. The fact that some substances are optically active, and rotate the plane of polarized light, was discovered by J. B. Biot (1774–1862), but the chemical significance of this fact was first brought out by L. Pasteur (1822–1895). In 1848 he found that one substance, tartaric acid, could exist in three varieties, as dextro, or right rotating, as lævo, or left rotating, and as racemic or optically inactive.

Optical Symmetry. He found that the racemic variety could be separated into two optically active parts, one dextro, and the other lævorotary, and that the lævo substance rotated the plane the same angle to the left as the dextro variety rotated it to the right. This has been found to be true of all substances separable into two optically active varieties and is called optical symmetry.

Methods to Separate the two Optically Active Varieties. Pasteur discovered and applied all the methods which we know even to this day for separating a substance into its optical isomers, as they are often called. His methods are four in number, as follows:

By Selecting Crystals. Substances which are optically active and which crystallize well are found in what are known as enantiomorphous forms; *i.e.*, showing some unsymmetrical crystal surfaces which make the two crystals appear as mirror images of each other. This particular lack of symmetry is known in crystallography as tetartohedry. Little surfaces appear, on a hexagonal prism, in a succession of positions which remind one of the threads on a right-handed

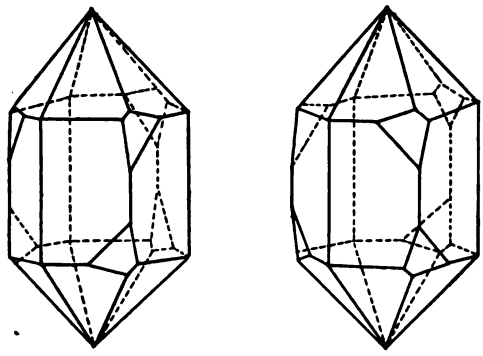


Fig. 29.

screw. Search will enable us to find exactly similar crystals, only with these little faces arranged in a way reminding us of the threads on a left-handed screw. These crystals cannot be placed in such a way as exactly to cover each other; one is to the other as an object is to its mirror image, or as a right-hand glove is to a left-hand glove. Enantiomorphous crystals of quartz are sketched in Fig. 29.

We may pick out a number of "right-handed" crystals and a number of "left-handed" crystals of tartaric acid. Making solutions of these we shall find that one solution is dextrorotary and the other lævorotary.

By the Formation of Derivatives. Derivatives of optically active substances with optically inactive substances are also active, and their properties agree with those of the original substances. But derivatives with another optically active substance frequently have different properties, for instance, different solubilities. Sodium

hydroxide is not optically active, and sodium salts of tartaric acid agree in their optical and other properties with the acids from which they were formed. But cinchonine, an optically active alkaloid, having the empirical formula $C_{19}H_{22}N_2O$, and having basic properties, may be used, and the derivatives of right-rotating tartaric acid with this base have a different solubility from the derivatives of left-rotating tartaric acid with this same base.

If we add cinchonine to a boiling solution of racemic tartaric acid, the cinchonine salt of the lævo acid crystallizes out first. The cinchonine may be displaced by ammonium hydroxide, and when this product is treated with dilute sulphuric acid we obtain pure lævo tartaric acid.

By Crystallization. A supersaturated solution of the racemic substance is made, and then crystallization is started by means of a minute crystal of one variety, say the dextro acid, and then only dextro crystals will separate out. If the crystallization be started with a minute crystal of the lævo variety, only lævo crystals will separate out. This is an interesting fact.

By Certain Ferments. Pasteur found that certain ferments, lower vegetable organisms, thrive in solutions of racemic substances at the expense of one variety, not touching the other. Thus it is possible to destroy one of the optical isomers leaving the other.

These four methods represent practically all that we know regarding the separation of a racemic substance into optical isomers.

Stereochemistry. Pasteur was the first to say that there must be some connection between optical activity and the positions of the atoms in the molecule, but the hypothesis as to what this connection might be was first formulated simultaneously in 1874 by Le Bel and van't Hoff. Their work may be considered as the beginning of what we call stereochemistry, the chemistry of space, (derived from the Greek word στερεός, meaning a solid).

The Asymmetric Carbon Atom. Every optically active substance was supposed by Le Bel and van't Hoff to have at least one carbon atom, each of whose valences was satisfied by a different group. The formula for tartaric acid may be written, $C_2H_3O_3{-}\overset{\displaystyle H}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}{-}CO_2H$, so conforming to this theory. This central C is called an asymmetric carbon atom.

If we consider all four valences of a carbon atom as alike, the

simplest geometric form to represent the atom is a tetrahedron. If something different is at each of the four apices, we can arrange them in such a way that two tetrahedra shall be mirror images of each other, as shown in Fig. 30. These two solid objects cannot by any twist or turn be brought to such a position that the same letters fit over each other.

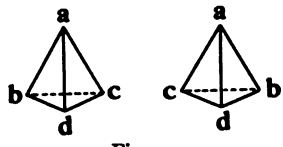


Fig. 30.

Compensation within the Molecule. There are two asymmetric carbon atoms in tartaric acid as is evident when we write the formula as follows: $HO_2C-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-CO_2H$. It is perfectly possible to imagine these as so arranged that the optical activity of one is just neutralized by the opposed optical activity of the other, to imagine, in other words, a compensation within the molecule. Such a tartaric acid could not be separated into two optically active varieties.

It is interesting evidence in favor of our theories that such a tartaric acid, a fourth variety, does actually exist, and is known as meso-tartaric acid. It is inactive, and has resisted all our efforts to split it into right- and left-rotating varieties. But it has the same number of atoms of the same elements, and the same molecular weight, and in all other respects acts like any other tartaric acid.

Other Asymmetric Atoms. Until within the last few years it was thought no substance could be optically active in solution unless it contained at least one asymmetric carbon atom. But compounds of tin, sulphur and nitrogen have been found possessing this property, and we have concluded that other atoms besides carbon may be asymmetric.

Asymmetric Molecules. More recently still some substances, apparently containing no asymmetric atom of any sort, have been found which, nevertheless, rotate the plane of polarized light. Such a substance is inosite (1 – methyl cyclohexylidene – 4 – acetic acid) the formula for which is written, $CH_3CH\begin{matrix}\diagup CH_2CH_2 \diagdown \\ \diagdown CH_2CH_2 \diagup\end{matrix}C=CHCOOH$. It may be separated into optical isomers by the cinchonine derivative method.* The suggestion has been made that the molecule

* W. Marckwald and R. Meth, *Berichte d. chem. Ges.*, **39**, 2404 (1906).

as a whole is asymmetric, exists, let us say, in enantiomorphous forms.

It should be added that many substances having asymmetric carbon atoms, according to their structural formulæ, are not optically active. But perhaps this means we have not yet succeeded in discovering the appropriate method for separating the racemic substance into its two varieties.

Molecular Rotation. Efforts to find some additional meaning in the observed facts by expressing them in terms of chemical units have failed. No regularity connecting the molecular rotation with the molecular weight is known, and any such connection is hardly to be expected because the property is so decidedly constitutive. But still, it cannot be wholly constitutive, for if it were, every asymmetric carbon atom should produce exactly the same effect, which is not the case.

It is evidence in favor of the electrolytic dissociation theory that dilute solutions of all salts of one active acid with inactive bases have the same rotating power. The plausible explanation for this fact is that all these salts, dissociating in water solution, give different cations, but always the same anion, and it is the anion which is endowed with the power to rotate the plane of polarized light.

Electromagnetic Rotation. It was found by Faraday in 1846, that a substance, itself not optically active, put in a strong electric field, say between the poles of an electromagnet, or within a spool of wire, acquired the power of rotating the plane of polarized light passing through it. This effect is then a property of the electrical field, rather than of the particular substance employed.

There is an essential difference between the rotation we have been describing and that produced electromagnetically. No matter in which direction we look through an optically active substance, the rotation is in the same direction relative to ourselves, just as if we look at one end of a screw and then turn it around and look at the other end. But in the case of electromagnetic rotation, it does make a difference which end we look at. From one end we see right rotation, from the other left. This is comparable to the way fur lies on a muff; looking at one end, the fur lies in the direction of the movements of the hands of a watch, looking at the other, it lies in the opposite way.

Perkin has shown that in each homologous aliphatic series the amount of rotation produced by a constant electric field increases a

definite amount for each addition of CH_2. In aromatic series the constitution of the substance has influence enough to complicate the results and prevent us from stating any simple regularity.*

* The authority on all questions relating to the topic of this chapter is, "The Optical Rotating Power of Organic Substances and its Practical Applications," by H. Landolt, translated by J. H. Long, 751 pp. This book contains very many references to the original literature.

CHAPTER XVIII

SOLUTIONS — III

SOLID SOLUTIONS

As was stated in Chapter XV, isomorphous crystalline substances are capable of forming mixed crystals. These mixed crystals are chemically and physically homogeneous throughout, and the proportions of their components may be altered gradually without causing an abrupt change in any property. They thus conform so perfectly to our definition of a solution that van't Hoff called them solid solutions.*

Solutions of Solids in Solids. These mixed crystals have been classified in four groups.

1. The substances are miscible in all proportions and may be said to furnish instances of true isomorphism. For example, $ZnSO_4.7H_2O$ and $MgSO_4.7H_2O$.

2. The two substances are miscible within definite limits, much as ether is soluble in water, and water is soluble in ether to certain different and limited extents. In such cases there is an appreciable difference between the crystal angles, and yet such substances also are considered as instances of true isomorphism. Pairs of substances which behave in this way are $KClO_3$ and $TlClO_3$, $BaCl_2.2H_2O$ and $SrCl_2.2H_2O$.

3. The two substances are not isomorphous, but yet mix in almost all proportions. For instance, $NaClO_3$ and $AgClO_3$.

4. The two substances, not isomorphous, mix only to a very limited extent. For example, KNO_3 and $NaNO_3$.

Isodimorphism. Cases falling in groups 3 and 4 are spoken of as instances of isodimorphism. Each of the pair of substances is capable of occurring in two crystal forms; one, its usual, the other an unusual form, the unusual form of one being the usual form of the other. Small quantities of one substance appear to be forced, as it were, into such unusual crystal form in order to become isomorphous with the

* *Zeitschr. f. phys. Chem.*, 5, 322–339 (1890).

other substance, which is present in large quantities, and to form mixed crystals with it.

Double Salts. Double salts are not to be classed as mixed crystals or solid solutions, for they contain their constituents in stoicheiometric proportions which cannot be gradually altered without producing abrupt changes in some properties. For the same reason, crystals containing water, alcohol, ether, etc., of crystallization are to be considered as chemical compounds rather than as solutions.

Solutions of Liquids in Solids. Certain silicates, the zeolites, contain indefinite quantities of water and are transparent and homogeneous throughout. Portions of this water may be removed gradually without causing any abrupt change. The water so driven out may be replaced by alcohol, ammonia, carbon dioxide, hydrogen sulphide, sodium silicate solution and other substances without destroying the transparency or appearance of homogeneity of the mineral. These zeolites furnish, then, an illustration of a solid solution with a liquid solute.*

Solutions of Gases in Solids. Instances of a gas dissolving to any marked extent in a solid are not so very frequent, but certain examples are striking and well known. Platinum and palladium take up large volumes of hydrogen (palladium a thousand times its volume and more), which must be considered as in solution in the metal. We say the gas is occluded or absorbed.

Diffusion in Solids. Hydrogen diffuses within platinum or palladium until it is homogeneously distributed throughout the metal.

That hydrogen will dissolve and diffuse in iron was proved as follows: The top of a barometer tube was closed by an iron plate which was then made the cathode of an electrolytic cell. When a current was passed through the cell, the mercury in the barometer tube fell, indicating that hydrogen passed through the iron.

It has been demonstrated that oxygen and nitrogen will pass through glass tubes when the temperature is high enough to somewhat soften the glass† and that oxygen will pass through quartz tubes at 600°.‡

Carbon diffuses into hot iron and through porcelain crucibles.

* W. Ostwald, "Grundriss der Allgemeinen Chemie," p. 372. F. Zirkel, "Elemente der Mineralogie," p. 733.

† Berthelot, *Compt. Rend.*, 140, 1159, 1286 (1905).

‡ Belloc, *ibid*, 140, 1253 (1905).

Gold diffuses into lead rather rapidly at temperatures a little below the melting point of lead, and perceptibly, in the course of a year, at room temperatures.* Copper-plated zinc gradually becomes lighter in color, due to the diffusion of zinc into the copper forming brass.

As diffusion in these cases is, so far as we can see, entirely analogous to the diffusion of gases into each other, or of a solute through a liquid solution; and as, while diffusion is in progress, we have mixtures homogeneous throughout, not containing their constituents in stoicheiometric proportions, mixtures the proportions of whose constituents may be altered gradually without producing any abrupt change in properties, we call them solid solutions.

When barium sulphate and sodium carbonate are pressed together, metathesis occurs, resulting in the formation of some barium carbonate and some sodium sulphate until a condition of equilibrium is reached between these four substances. This behavior is characteristic of solutions. We are inclined to believe that whenever two solids enter into chemical reaction they first dissolve in each other, the idea being that they could not otherwise get near enough together for chemical affinity to come into play. This may, however, be a survival of the opinions of the old alchemists which they expressed in their saying: "Corpora non agunt nisi soluta."

Diffusion Does not always Occur. That diffusion does not always occur between solids, even when they are strongly pressed together for geological ages, is demonstrated by many well-known minerals, for instance, by banded agates.

Alloys. Some alloys conform to our definition and must be considered as solid solutions; others contain their constituents in definite parts by weight and so must be considered as chemical compounds.

Hardened steel is looked upon as a homogeneous solid solution of carbon in iron, and is called martensite; while not hardened steel is probably a mechanical mixture of pure iron and carbide of iron.

Glass and Dyed Fibers. It is not customary to include colored glasses in the category of solid solutions, for glass, being amorphous, is generally classed as a liquid of great viscosity. Opinion is divided as to whether the coloring matter in the fibers of a dyed fabric is to be considered as in solid solution or not. Colored glass and dyed fibers are probably most properly regarded as colloidal solutions of great viscosity.

* Roberts Austen, *Proc. Roy. Soc.*, **67**, 101 (1900).

Osmotic Pressure in Solid Solutions. Since diffusion occurs in solid solution there must be a force causing it. It is reasonable to consider osmotic pressures as due to the force causing diffusion, and therefore we may imagine osmotic pressures as existing in solid solutions. There is practically no chance of our ever finding a semipermeable membrane applicable here, and therefore direct measures of maximum osmotic pressures in solid solutions are probably forever beyond our reach.

Indirect measures, however, may be discovered. It is reasonable to suppose there is a connection between osmotic pressures and internal pressures in solids, and that the latter are connected with the property of hardness. Thus we may some day establish a quantitative relationship between hardness and osmotic pressure. Osmotic pressure being a colligative property, this would give a method for determining molecular weights of solids.

We know that silicon and other substances when dissolved in iron increase its hardness, and it has been shown that equivalent quantities of different solutes, as carbon and silicon, produce the same change in hardness.* Moreover, equivalent quantities of different solutes appear to affect the electrical conductivity of solid solutions to the same extent. So we have made a beginning on a method for determining molecular weights of solids, but these indications have not yet been developed to a satisfactory degree of reliability.

Adsorption. Solids are able to condense gases, liquids, or dissolved solids on their surfaces. As long as these gases, liquids, or dissolved solids remain on the surface and do not penetrate to the interior they are said to be adsorbed. Adsorption is then a manifestation of the force we call adhesion. If they penetrate, they are said to be absorbed or occluded, and in some cases, as we have seen, we consider them as in solution, in other cases as in chemical combination. A solid may both adsorb and absorb a gas and in such case it is not easy to determine to what extent each process has occurred.

Adsorption of Gases. The usefulness of charcoal as a deodorant is due to its ability to adsorb gases. One cm^3 of charcoal at 0° takes up 4 cm^3 of hydrogen or 18 cm^3 of oxygen; at $-185°$, the temperature of liquid air, it takes up 135 cm^3 of hydrogen or 230 cm^3 of oxygen.† Adsorption is thus greater the lower the temperature.

The following is a familiar experiment: A piece of platinum or palla-

* C. Benedicks, *Zeitschr. f. phys. Chem.*, **36**, 529–538 (1901).

† J. Dewar, *Chem. News.*, **94**, 173–175 (1906).

dium foil is held in a bunsen flame until red hot. The gas is turned out and the foil cools. The gas is turned on again and allowed to play on the foil which then begins to glow and finally relights the gas. The hydrogen in the water-gas is absorbed and adsorbed, both of these processes evolving heat. Thus condensed the hydrogen unites more rapidly with the oxygen of the air, and this reaction contributes more heat, until finally the kindling temperature of the gas is reached.

Welsbach Mantle. The remarkable efficiency in converting heat into light shown by the Welsbach mantle has been ascribed to the power for adsorption (or absorption, or both) of the oxide of cerium it contains.

Heat Evolved during Adsorption. Adsorption results in the evolution of heat, for it involves the condensation of the adsorbed gas, but in many cases the heat evolved is more than can be accounted for in this way. For instance, palladium, in taking up a thousand times its volume of hydrogen, increases in volume more than 1.5 per cent and evolves about 4000 cal. for each gram of hydrogen so taken up. There is reason for assuming that we have adsorption, solution, and chemical combination, all three occurring.

The conditions are similar with platinum, silver, copper, and iron, which take up smaller volumes of hydrogen or oxygen.

Catalytic Effect of Metals. There is no doubt but what a part of the gases is held as a condensed layer on the surface, in which condition, very much concentrated, it reacts faster. This is a plausible explanation for the notable increase in the velocities of many reactions between gases in contact with finely divided platinum or other surfaces.

Adsorption of Liquids. Layers of liquids often adhere firmly to solids. The tenacity with which a film of water will cling to glass vessels is a source of error hard to avoid in making accurate weighings. This was pointed out in Chapter III in connection with the descriptions of Landolt's experiments.

Whether a given solid is "wet" or is not "wet" by a given liquid is a question of adsorbing power, and thus this phenomenon is closely connected with capillary phenomena.

It has been shown that when a finely powdered insoluble substance is wet there is an evolution of heat. This is probably due to the compression of the liquid by the force of adhesion causing the adsorption.

Adsorption of Dissolved Substances. A few drops of a solution of barium hydroxide are allowed to fall in one spot on a piece of filter paper. Adjacent, but outside the wet ring, a few drops of a solution

of phenolphthaleïn are put on the same filter paper. The wet rings, increasing in circumference, soon overlap, but they overlap some distance before the characteristic red color of the indicator appears. This simple experiment shows clearly that the filter paper adsorbs the reagents from their solutions until the outer portions of the wetness consist of such dilute solutions that they cannot show even this delicate reaction. Owing to this behavior of filter paper the first five or ten cm^3 of the filtrate should always be thrown away when making up solutions of definite concentrations.

It is an interesting fact that a given amount of sand has been found to adsorb equivalent quantities of the solute from equivalent normal solutions of many salts.*

It has been suggested that when a solid is in contact with a solution there is always a layer of solvent in a high state of compression next the solid. Now if the solubility of the solute is greater the greater the pressure, that layer will be more concentrated; if the solubility is less the greater the pressure, that layer will be more dilute than the rest of the solution.

The phenomena dealt with in this chapter may be thought to be of minor importance, but they are not. More and more we are realizing that the conditions in contact surfaces often play the decisive rôle in important processes. To understand and control those processes we must know those conditions.

* G. C. Schmidt, *Zeitschr. f. phys. Chem.*, **15**, 56–64 (1894).

CHAPTER XIX

SOLUTIONS — IV

COLLOIDAL SOLUTIONS

So many new and significant facts have been gathered within recent years under the title "Colloidal Chemistry" that it is beginning to be treated as a special branch of our rapidly growing science, and has textbooks and a journal of its own.* It comprises much of the chemistry and physics of life processes and therefore it is one of the most interesting parts of physical chemistry to those engaged primarily in other sciences. The possibilities of future discoveries in this province are alluring.

Historical. The facts are by no means all new. In 1862, Thomas Graham (1805–1869) observed that such substances as common salt, copper sulphate, potassium nitrate, etc., diffuse through a parchment membrane almost as rapidly as if no membrane is present, while such substances as gelatine, agar-agar, gum arabic, etc., hardly diffuse through a parchment membrane at all.

Crystalloids and Colloids. The latter substances are gummy, sticky, and he called them colloids, indicating by this name their mucilaginous nature. The former substances all form well-defined crystals, and he called them crystalloids, in contradistinction to colloids.

Dialysis. Upon this difference in properties he based a method of separation (analysis) which he called dialysis. He stretched a piece of parchment over a hoop, so making what he called a dialyzer. He placed a solution containing both a crystalloid and a colloid inside and floated the apparatus on distilled water. Anything of a crystalloidal nature diffuses rapidly through to the distilled water, while

* "Colloids and the Ultra Microscope." by Richard Zsigmondy, translated by Jerome Alexander, 245 pp. (1909); "Grundriss der Kolloidchemie," by Wolfgang Ostwald, 525 pp. (1909); "Kapillarchemie," by H. Freundlich, 591 pp. (1909). *Zeitschrift für Chemie und Industrie der Kolloide.*

anything of a colloidal nature passes through so slowly that the amount is practically negligible, and thus separations are effected.*

Dubrunfaut devised dialyzers to remove objectionable materials from molasses obtained in the manufacture of sugar from beets eight years before Graham published his articles.† It is curious and unjust that Graham should receive so much credit and Dubrunfaut so seldom any.

Other Membranes. Other substances act in the same way as parchment and parchment paper. Collodion membranes are particularly convenient as they can be made as wanted in great variety of thickness and form; as flat sheets by pouring collodion on mercury (thus ensuring a level surface), as sacks, by coating test tubes.‡

Many animal membranes are used, for instance, gold beater's skin, which is the lining of the peritoneal cavity of a calf, bladders, and heart sacks. As was said in our discussion of osmosis the whole body is made up of organs and cells surrounded by membranes which permit the passage of some dissolved substances and hinder or prevent that of others. Digestion and secretions by glands are in great measure instances of such selective diffusions. If the nature of these membranes alters, the animal economy is affected, and doubtless such alterations are often the cause of illness.

Other Colloids. There are two parts to Graham's definition of a colloid: first, when it is pure, or mixed with little water, it is like a gum and sticky; second, when it is in solution it will not diffuse through parchment, or a similar membrane. The first part of the definition was soon disregarded and the second part was adopted as the sole

* A great variety of experiments have been devised to illustrate dialysis; the following two are convenient for lecture demonstrations. *A*. Put a solution of KCNS inside a dialyzer; after it has floated on distilled water for one to two minutes, add $FeCl_3$ solution to the distilled water outside. The red color demonstrates that the crystalloidal potassium thiocyanate passed readily through the parchment membrane. *B*. By mixing equal volumes of $\frac{n}{50}$ $FeCl_3$ and $\frac{n}{50}$ $K_4Fe(CN)_6$, we obtain a colloidal solution of prussian blue, so dense in color that it can be seen through only in thin layers. Place some of this in a dialyzer and no perceptible trace of the color gets through the membrane in hours. (See A. A. Noyes, "The Preparation and Properties of Colloidal Mixtures." *Jour. Am. Chem. Soc.*, **27**, 85–104 (1905), for this and other interesting demonstrations.)

† See the introduction to "L'Osmose et ses applications Industrielles," by Dubrunfaut, Paris (1873), 250 pp., for discussion and references regarding priority.

‡ For details as to these manipulations, see Bigelow and Gemberling, "Collodion Membranes," *Jour. Am. Chem. Soc.*, **29**, 1576–89 (1907).

criterion; and it is indeed the more important of the two properties. Whether a substance is sticky or not, if it does not diffuse through parchment membranes, we call it a colloid.

The question at once arises, why will some substances pass through these membranes while others will not? The simplest assumption possible is the most plausible we have. The membranes are probably networks of fine capillaries. If the particles of the solute are larger than the holes in the membrane, they will not go through; if smaller, they will.

Effort to Delimit Colloidal Solutions. And so, whether a substance is to be called a colloid or not is to be determined by the size of its particles when in solution. At one extreme we have what we please to call true solutions, such as those already mentioned, solutions of common salt, sugar, copper sulphate, etc. At the other extreme, we have what we call suspensions, such as we can make by shaking up fine sand and water. We can see the separate particles in suspensions and we know that in time they settle out. But the finer the particles, the longer it takes them to settle out, and if only they are fine enough, it will take an infinitely long time for them to do so. If oil be shaken up with water an emulsion results, cloudy and more or less opaque, owing to the great number of minute oil globules in suspension. The oil separates in the course of time, but some emulsions contain such very fine globules the time required for separation may be days, weeks, even years. There is a perfect continuity from one extreme to the other, and it is by no means easy to draw lines between suspensions and colloidal solutions on the one hand, or between colloidal and "true" solutions on the other. In fact, no one as yet has done it entirely satisfactorily.

Present Usage of the Terms. We are inclined to apply the term suspension if any indication of settling out is perceptible after a short time, or if we think separation will eventually take place. We apply the term colloid if we think no settling out will occur in a long while, and continue to apply it to combinations with increasing fineness of grain until we can no longer distinguish the particles of solute from the circumambient solvent with the best microscopes, or by the ultramicroscopic method. Then, finally, we apply the term "true," or ordinary, solution. There is no natural and necessary boundary on either side, and it is at least reasonable to suppose that a "true" solution, magnified more than we now know how to magnify it, would look just like the solutions we call colloidal. At present, then, we

include under the head of colloids substances dispersed through a solvent in particles so fine they will not settle out, and yet not so fine but what we can, by experiment, form approximate estimates of their sizes.* That we can go far with these estimates will presently appear.

Hydrosol and Hydrogel. If we dissolve four grams of agar-agar in one hundred grams of hot water, the solution is as liquid as water at 70°, but upon cooling to room temperature it "sets" to a jelly. The same behavior is shown by gelatine and numerous other, but not all, colloids. While a mobile liquid the solution is called a hydrosol, when "set" it is called a hydrogel, often abbreviated to "gel." For colloidal solutions wherein the solvent is ethyl alcohol, the terms alcosol and alcogel have been coined, but they are seldom used and superfluous. The "setting" of plaster of Paris, of mortar, of Portland cement, and of currant jelly are doubtless analogous phenomena.

Diffusion through Hydrogels. Some of these "gels" act like parchment membranes, permitting the diffusion of crystalloids almost as if the colloid were not present, but hindering, or practically preventing, the passage of other colloids. On the basis of these facts we turn about and say that any membrane which permits the passage of a crystalloid and hinders the passage of a colloid is itself a colloid.

Structure of "Gels." These "gels" have a sponge or honeycomb structure and take up and hold large quantities of liquid solvent by capillarity. Possibly the pores are large enough to permit the passage of the smaller crystalloid particles readily, but not large enough to permit the passage of the larger colloid particles. The assumption of pores and a sieve action is plausible in all cases.

Applications. These principles have several important technical applications. "Dry batteries" may be made by gelatinizing the liquid contents. The electrolyte diffuses unhindered from one electrode to the other, and yet, even if the battery is inverted, no liquid will run out. The sensitive films on "dry plates" are jellied colloidal solutions of the silver halides in gelatine. When in the developer the reducing agent diffuses readily throughout the mass, but the colloidal silver cannot diffuse through the jelly and remains in position. If it were not for this, there could be no such thing as "sharp definition" in a negative. Smokeless powders, blasting gelatine, cordite, etc., are gelatinized solutions of nitroglycerine. When gelatine is used to hold the liquid nitroglycerine in convenient forms, it acts as a diluent,

* Wolfgang Ostwald advocates abandoning the term colloid and substituting the term "dispersed system."

diminishing, as desired, the suddenness of explosions. Nitrocellulose (gun cotton) may be used in place of gelatine and this gives our high explosives. Many processes of dyeing are illustrations of the same principles. The fibers act as membranes, *i.e.*, are colloidal in nature. The dye enters as a crystalloid, is converted to a colloid, and then can no longer come out; it becomes a "fast" color. Bacteriology could not have attained its present development and value without the gelatinized solutions of gelatine and agar-agar upon which cultures are made and colonies of bacteria are nourished yet kept apart.

Coagulation. Some colloids do not form jellies, but coagulate. Make an approximately one per cent solution of arsenious oxide (As_2O_3) by boiling an excess of the solid for about fifteen minutes in water. When cool, add an equal volume of water saturated with hydrogen sulphide. The result is a yellow colloidal solution of arsenious sulphide which will pass unchanged through filter paper, but many individual particles of the sulphide can be seen when the solution is inspected by the ultramicroscope. Add to this colloidal solution a small amount of a solution of hydrochloric acid or of magnesium chloride, or of any electrolyte whatever, and the sulphide collects in flakes which soon settle, or will be retained by filter paper. Experiment has taught us that many colloids are thus coagulated by solutions of electrolytes. An electrolyte containing a bivalent ion is much more effective than one containing a univalent ion, and one containing a trivalent ion is much more effective than one containing a bivalent ion. We have no adequate explanation of this interesting generalization.

Milk is a colloidal solution. When it turns "sour," acids have formed and these, being electrolytes, coagulate the colloids. Rivers bring many substances in colloidal solution with them. When they empty into the ocean, which is a solution of an electrolyte, sodium chloride, these colloids are coagulated and precipitated, forming the extensive deltas at their mouths.

Heat often produces coagulation as in the case of albumin, and for many substances there appears to be a definite temperature of coagulation, but this is often obscured, for, if an electrolyte is present, the temperature necessary for coagulation is usually lower. The phenomenon of coagulation is frequent and important and it is to be hoped we shall soon know more of the underlying principles and causes.

Agglutination. Bacteria in a liquid act in many respects like colloids and may be coagulated; the term used in this connection is "agglutination." What is known as Widal's test is an interesting application of these principles for the diagnosis of typhoid fever. Typhoid bacteria produce, as a product of their life process, what is known as an agglutinine serum which agglutinates (coagulates) typhoid bacteria. This is specific, that is, this serum will not agglutinate other bacteria. Serum obtained from the patient suspected of having the fever is added to a liquid containing typhoid bacteria. If the bacteria are agglutinated, the patient has typhoid; if they are not, the patient probably has not typhoid fever. Serum therapy and the chemistry of the toxines and antitoxines are full of instances such as this.

"Protecting" Colloids. Coagulation can be retarded or entirely prevented. Mix equal volumes of $\frac{n}{20}$ $AgNO_3$ and $\frac{n}{20}$ NaCl, and the silver chloride forms flakes and settles as a precipitate almost at once. Repeat the experiment, only using a sodium chloride solution containing rather more than one per cent of gelatine. An opalescence appears, a property characteristic of the presence of fine particles, and grows slowly more pronounced, showing that silver chloride has formed; but precipitation does not occur. The gelatine acts as a "protecting" colloid, as it is called. It is generally assumed that the first small particles of silver chloride to form attract coverings of gelatine to themselves. Inasmuch as colloids cannot diffuse through colloids, these small particles cannot get together to combine and form particles large enough to settle out, and so remain in "colloidal solution." This is the most probable hypothesis yet advanced to account for the facts, but this mechanism of a protective coating cannot be said to have been convincingly demonstrated by experiment in all cases.

The behavior described is of much importance in the art of photography; it makes our dry-plate processes possible. Silver chloride in an extremely finely divided state is not particularly sensitive to light, but as the particles grow larger, they become more sensitive. When large enough, a very short exposure reduces them, in part at least, to a lower oxide or to metallic silver. Where this action has been started it proceeds more readily than elsewhere, and the developer, which is nothing but a gentle reducing agent, develops the negative in metallic silver. If the particles of silver chloride are

large enough, the reduction proceeds of itself, without previous exposure to light, in the dark. In making dry plates, silver bromide is precipitated in solutions containing gelatine and then the emulsion, as the resulting colloidal solution is called, is ripened; *i.e.*, the particles of silver chloride are caused to grow larger. This they will do gradually, for the electrolytes, silver nitrate and sodium bromide can diffuse through the colloidal coating of gelatine though the colloidal silver bromide cannot. Diffusion is slow at ordinary temperatures, but is much hastened by heat; therefore the emulsion is warmed. Experience has taught how far to continue this " ripening " process to bring the colloidal particles just up to, but not over, the threshold. Our sensitive dry plates and films consist of glass plates and celluloid sheets coated with such " ripened " emulsions.

Coagulation May Be Reversible or Irreversible. Some hydrogels will redissolve to form the original hydrosols and others will not. Gelatine is typical of the first kind, called reversible, and arsenic trisulphide is typical of the second, called irreversible. A reversible hydrogel may be made irreversible; for instance, if we evaporate the water from a colloidal solution of silicic acid at a low temperature we obtain a glass like hydrogel which will redissolve in water to give back the original hydrosol. If we drive off the water and heat rather strongly we render the silicic acid practically insoluble.

Traces of other substances often suffice to convert a hydrogel to a hydrosol. Graham found that one part of sodium hydroxide in ten thousand greatly facilitated the conversion of silicic acid " gels " to " sols."

Colloidal Metals. Colloidal solutions of metals are particularly interesting, for it is rather surprising that we can divide a heavy metal into such fine particles they will not settle out. Faraday made colloidal gold solutions some years before Graham invented the name. He put small pieces of yellow phosphorus into dilute solutions of chloride of gold, which, by this means, is slowly reduced, giving particles of metallic gold so small they do not settle. The colors of these colloidal gold solutions vary all the way from a rich ruby red through all shades of purple to an equally rich blue. These solutions show the phenomenon of dichroism; displaying two colors, one, that above mentioned when observed by transmitted light (a source of light or a white background is looked at through them), and a second, in this case a warm brown, when observed by reflected light (the source of light and the observer are on the same side of the solution).

Whether red or blue, the solution owes its color solely to the presence of fine particles of metallic gold, and it is indeed remarkable that there should be such a wide color range. Different views have been held as to the cause of the differences in color. Any electrolyte will turn a red gold solution blue. Electrolytes, in general, cause the particles in a colloidal solution to grow larger until they get so large they settle out, or coagulate. So it is reasonable to conclude the red solutions contain the finer particles, and that the color is determined by the average size of the particles. Best quality ruby glass is a colloidal solution of metallic gold in glass.

There are numerous methods of obtaining colloidal gold solutions, but they are all the same in principle, depending on the action of a mild reducing agent, such for instance as formaldehyde, on a solution of gold chloride.

G. Bredig devised an entirely new method by which we can obtain a colloidal solution of practically any metal in practically any solvent in a short time. His method consists in establishing an arc (somewhere about 100 volts and 6 to 8 amperes) between electrodes of the chosen metal beneath the surface of the chosen solvent. Clouds of metal particles puff out from the cathode, and while some settle out almost at once, others are so minute they remain suspended indefinitely. This is a pretty and easily carried out experiment. The process is not merely a mechanical pulverization of the metal, but it is also largely an electrical phenomenon, and has points of similarity with the emission of cathode rays and of electrons.

Ultramicroscopic Method. Exceptionally ingenious work has been done in determining the probable size of the particles in colloidal solutions. Our best microscopes enable us to distinguish a line from 0.5 to 0.1 micron in width, and with such an instrument we can see and count the particles in many colloidal solutions. It is possible to make yet smaller particles visible by what has been aptly named an ultramicroscopic method.

Tyndall Effect. If a beam of light passes through a room containing dust, and we look in a direction at right angles to the beam, we see it clearly outlined, for each dust particle reflects light to the eye. If the room is entirely free from dust we see nothing whatever; such a space is spoken of as optically empty. If the space contains exceedingly fine particles, the path of the light beam looks blue. This is why the sky looks blue, for the sun's rays strike countless exceedingly fine particles of dust, and at higher altitudes doubtless

minute globules of condensed gases, and at all elevations molecules of the constituent gases, and are thus reflected to our eyes. These particles are relatively near the surface of the earth, for soon after sundown the sun's rays, passing somewhat higher overhead, meet nothing to reflect them, and so the sky looks dark. This visibility of beams of light through the agency of fine particles is known as the "Tyndall effect."

Siedentopf and Zsigmondy* send a powerful beam of light, projecting the image of the sun or of an arc light, by means of a microscope, into a colloidal solution, and then look at this image in a direction at right angles to the path of the rays through another powerful microscope. This combination is what is known as the "ultramicroscope." In this way particles much too small to be seen by direct vision methods betray their presence by the light they reflect. Colloidal solutions are seen to be swarming with fine particles while true solutions appear optically empty.

With the ultramicroscope it is possible to count the number of particles in a given small volume of, let us say, a colloidal gold solution. By analysis, we can determine the weight of gold present per unit volume, and so the weight of gold present in the volume in which we have counted the number of particles. Thus we can calculate the average weight of each particle. Assuming their specific gravity to be the same as that of larger masses of the metal, we may calculate the volume of one. Assuming the particles to be spherical, we can calculate their diameters. Perhaps these assumptions are not strictly justifiable; then corresponding errors are introduced in the results. The claim is not made that the dimensions so reached are accurate and final, but at least they must be fair approximations, and give the order of magnitudes involved.

Size of Particles. The smallest particles which have been counted by the above method are those in a red colloidal gold solution, and their diameters have been calculated as 6 $\mu\mu$ (millimicrons). Of course other colloidal gold solutions contain larger particles, ranging continuously all the way up to those which settle out rather quickly. This 6 $\mu\mu$ diameter is the smallest dimensioned object which has ever been seen and counted, and it will be a long while before we contrive a method to see anything smaller, for it is easy to calculate that an object with one-tenth this diameter would have to

* For full details see "Colloids and the Ultramicroscope," by Zsigmondy, referred to at the beginning of this chapter.

emit light with an intensity greater than that of the sun to produce an effect on our retinas. But one-tenth of this, or 0.6 $\mu\mu$, brings us to the order of magnitudes we are in the habit of ascribing to molecules, so we have succeeded in penetrating rather deep after all. Assume a cubical form for the gold particle; then it must contain at least $10 \times 10 \times 10 = 1000$ molecules, probably more.

Nomenclature. A nomenclature has been adopted for these small objects. Particles too small to be seen by the unaided eye, but visible under the microscope, say down to a diameter of 250 $\mu\mu$, are called microns. Particles too small to be seen with a direct vision microscope, but countable by the ultramicroscopic methods, with diameters then from about 250 $\mu\mu$ to about 6 $\mu\mu$, are called submicrons. Particles smaller than these, with diameters less than 6 $\mu\mu$ are called amicrons. Colloidal solutions then cover the range from the smaller microns to the amicrons. "True solutions" include the amicrons only. But, as has been said, there is no valid reason to suppose there is any abrupt change in passing from colloidal to "true" solutions.

Osmotic Pressures of Colloidal Solutions. Colloidal solutions exert very small osmotic pressures, in fact some maintain that they exert none. Osmotic pressure and rate of diffusion may be utilized to determine molecular weights. When such calculations are carried out for colloids, extravagantly large figures result. For instance, the molecular weight of starch appears to be about 25 000; of albumen, 14 000; of ferric hydrate, 6000; of silicic acid, 49 000. Caoutchouc in benzene shows a molecular weight of 6500, and tannin in glacial acetic acid a molecular weight of 1100.

The interesting investigations by J. Perrin of the Brownian movements of the individual particles in colloidal solutions have been referred to in Chapter XI. The behavior of these particles under the influence of an electrical potential gradient, producing the phenomenon called cataphoresis, will be described in Chapter XXVIII. The reader is referred to the texts cited at the beginning of this chapter for much information of necessity omitted here.

SECTION IV

PROCESSES

CHAPTER XX

LIQUEFACTION OF GASES

EVERY observation we make involves a series of processes, inasmuch as some form of energy transference or transformation is the necessary medium between our minds and the external universe. But thus far in this book our attention has been directed primarily to the study of properties as such, and we have excluded, so far as we conveniently could, consideration of the changes which occur in substances. With this chapter we begin a section wherein our attention shall be directed primarily to processes.

Different Kinds of Processes. A change, or process, consists of a redistribution of energy. This redistribution may be a transference of a quantity of a certain kind of energy from one place to another, or it may be a transformation of a certain quantity of energy of one kind into an equivalent quantity of another kind, or it may be partly one and partly the other.

In Chapter III we learned that all forms of energy may be classified under relatively few heads, and that these in turn offer a logical and convenient classification for the study of processes. On this basis we defined the contents of the subjects, thermochemistry, electrochemistry, actino (or photo) chemistry, and thermodynamics.

The study of a group of processes not specifically named in this classification has been most fruitful in furnishing great and useful generalizations. These are the processes wherein changes of aggregation occur, as in the liquefaction of gases, the vaporization of liquids, freezing and melting, the process of solution, and, we may add, changes of form in the solid state. Inasmuch as all these changes are accompanied by an evolution or absorption of heat, are either exothermic or endothermic, they constitute a subdivision of thermo-

chemistry. Some consider that changes of aggregation should be classed with physics rather than chemistry. To satisfy such demand we might coin a word and call them thermophysics. As has been said, our efforts at classification are at best imperfect, the continuity of nature is everywhere apparent, and we may catalogue them as we please, but one thing is certain, no chemist to-day can afford not to have a fair working knowledge of them. We shall therefore proceed to their discussion, laying stress on those features of particular significance in the science of chemistry.

The Liquefaction of Gases.* In 1823 Faraday began the experimental work which has finally culminated in the liquefaction of every known gas. The first substance (ordinarily obtained and studied as a gas) to be liquefied was chlorine. In a tube, bent at about a right angle, sealed at both ends, Faraday heated some of the crystalline hydrate of chlorine, $Cl.4\,H_2O$ (often written $Cl_2.8\,H_2O$). The empty end of the tube was in a cooling mixture, and here a greenish yellow liquid collected. Investigation proved it to be pure chlorine. The decomposition of the hydrate had furnished the pressure necessary for liquefaction.

Carbon Dioxide. In 1835 Thilorier liquefied carbon dioxide on a large scale. This liquid carbon dioxide, allowed to escape from a cylinder, cools itself sufficiently, owing to the sudden expansion, to solidify in part. This solid, snow-like material, mixed with ether, furnishes a ready means of obtaining a temperature of $-100°$. The ether has nothing to do with the low temperature reached and serves only to establish close contact between the carbon dioxide and the object to be cooled. The cooling effect is produced solely by the liquefaction and vaporization of the carbon dioxide.

The "Permanent" Gases. With the aid of this low temperature, Faraday continued his studies and finally liquefied all known gases, excepting hydrogen, nitrogen, oxygen, carbon monoxide, and methane. These five resisted his efforts, and on this account were known as the "permanent" gases.

Oxygen. In 1877 Pictet, boiling liquid sulphur dioxide in vacuo, cooled liquid carbon dioxide, which he then boiled under diminished pressure. By this means he reached a temperature of $-140°$ or lower. He generated oxygen from potassium chlorate in an iron retort while the receiver connected to the retort was immersed in this

* For an interesting account of this subject and much experimental detail see "Liquefaction of Gases," by W. L. Hardin (1899), 250 pp.

cold carbon dioxide. The chemical reaction furnished the necessary pressure, and in this way Pictet liquefied considerable quantities of oxygen.

Hydrogen. Simultaneously Cailletet subjected gases to very high pressures, gave them a preliminary cooling, and then opened the vessel suddenly. By this method of sudden expansion against atmospheric pressure he succeeded in liquefying not only oxygen, but also hydrogen.

Adiabatic Expansions. Where a process occurs in such a way that heat is neither given off by a system nor conducted into it, the process is said to be adiabatic. Of course these conditions cannot be strictly fulfilled experimentally, for some conduction is bound to occur, yet if the process occurs with sufficient rapidity, the amount of conduction must be small and it is very nearly adiabatic.

The expansions which Cailletet made use of were so sudden as to be practically adiabatic, and they produced such notable cooling effects upon the gases that mists were seen to form within the glass tubes in which they had been confined. The tubes were known to contain nothing else, therefore the mists must have consisted of small liquid particles of the gas. These mists were gone almost as soon as seen, and were nothing more than scientific curiosities, yet the fact remains that Cailletet liquefied hydrogen in 1877.

Critical Temperature. Natterer subjected air to pressures of thousands of atmospheres without observing the phenomena of liquefaction. Faraday and Cailletet recognized that pressure alone was not sufficient to liquefy a gas, and that it was necessary to cool it simultaneously, and that of the two the cooling was the more important. There is a temperature, definite but different for each gas, above which no pressure will cause it to separate into two portions or phases as we call them, one liquid, the other gaseous. This maximum temperature at which the phenomena of liquefaction may be observed is known as the critical temperature.

If a gas, above its critical temperature, be subjected to increasing pressures, ultimately the decrease in volume will correspond to the relative incompressibility of a liquid, but at no stage in the process is any lack of homogeneity observable in the body of the gas.

If a sealed tube half full of liquid, half full of gaseous carbon dioxide, be warmed gradually, the meniscus separating the two phases grows flatter and less distinct until at 31.8° it disappears. At temperatures above this, the contents of the tube are homogeneous.

If allowed to cool again, at 31.8° a cloudy band, like a smoke ring, appears in some part of the tube and immediately thereafter the bottom of the tube is obviously filled with liquid, the top with gas, and we have the two phases separated by a meniscus.*

Experimental Determination of Critical Temperatures. It is easier to determine the critical temperature than it is commonly supposed to be. Take a piece of ordinary glass tubing of internal diameter let us say 4 mm., with walls from 0.7 to 1 mm. thick, seal off one end carefully and 8 or 12 cm. from this draw it out to a capillary. Bend the capillary to a right angle and dip it in the liquid. By alternately heating and cooling draw liquid into the tube and by boiling displace all air. Seal off the capillary near the tube when the latter is from half to three-quarters full of liquid and the rest of the tube is full of the same substance as gas. Heat this tube slowly in an air bath or in some high boiling liquid until the meniscus disappears. Upon cooling the cloudy ring appears and the temperature at which this occurs is the critical temperature. Repeated observations with rising and with falling temperatures may be made with the same tube and the average of several may be taken as the critical temperature sought. As the tube may burst, the observer should take the precaution of placing a sheet of plate glass between himself and the experiment.

Critical Pressure. We may place a liquid under heavy pressure and then warm it. If the pressure exceeds a definite value characteristic of the substance, no matter to what temperature we raise it we shall not observe a separation into two phases, one liquid, one gaseous, separated by a meniscus. Therefore, there is a maximum pressure at which the two phases, gas and liquid, can exist in contact with each other. This is known as the critical pressure. Another way to define critical pressure is, the pressure which is just sufficient to produce liquefaction at the critical temperature.

Experimental Determination of Critical Pressure. A glass capillary about 30 cm. long, internal diameter about 1 mm., AB, in Fig. 31, is filled with the liquid to be investigated, confined by mercury as indicated. It is cemented into a metallic sleeve which forms

* At one time a distinction was drawn between the terms gas and vapor. A substance in the gaseous state was called a vapor when below its critical temperature, and a gas when above it. There is no advantage to be derived from maintaining this old usage; water vapor above water at 20° is a gas in all its properties just as much as the air in which it is dissolved.

a connection with a copper capillary leading to the pressure gauge *G* and the pump *P*. This pump is merely a metallic cylinder with a piston which may be screwed in. The cylinder, gauge, and capillary tubes are filled with paraffin oil. Heat the glass capillary and raise the pressure until the cloudy ring appears and disappears. Note the pressure on the gauge. Repeat several times and take the average of all the readings.

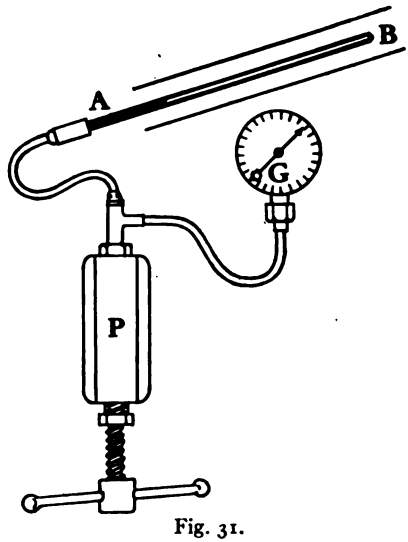


Fig. 31.

Critical Concentration. The gas laws are the expression of the interrelationship between the three variables, pressure, temperature, and volume. If the first two are fixed the third is likewise determined. Therefore a given quantity of a gas at its critical temperature and pressure must occupy a definite volume. This is called its critical volume. As the temperature rises a liquid expands, its density becomes less, its concentration (quantity per unit volume) becomes less. As the pressure increases the volume of a gas becomes less, its density (concentration) becomes greater. Thus when we have the two phases in contact and carry out the experiment just described, their concentrations become more and more nearly the same. When the critical conditions are reached the two concentrations (or densities) are the same. Thus we may define critical density or concentration as that density or concentration possessed by a substance when at its critical temperature and pressure. It is the same whether we consider the substance as a liquid or a gas.

It is sufficiently evident how we may utilize the apparatus shown in Fig. 31, to determine the critical concentration or density simultaneously with the other critical constants.

The actual facts are perhaps not quite so simple as this reasoning. Pinhead-sized bits of glass of different specific gravities were enclosed in a tube of carbon tetrachloride and this was raised to its critical temperature. The bits of glass floated at different levels, proving

the existence of different densities through a range of several degrees above the temperature at which the meniscus disappeared.* Perhaps the statement that the two phases become identical at the critical temperature is not strictly accurate.

Critical Constants. The following is a short table of some critical temperatures, pressures, volumes, and densities. t_c denotes the critical temperature on the centigrade scale. p_c denotes the critical pressure in atmospheres. v_c denotes the volume in cm^3 occupied at the critical temperature and pressure by a quantity of the substance which, as a gas, at 0° and 760 mm. would occupy one cm^3. d_c denotes the density based on water at 4° as unity.

	t_c	p_c	v_c	d_c
H_2O	364.3	194.61	0.003864	0.429
C_2H_5OH	243.6	62.76	0.00713	0.288
$(C_2H_5)_2O$	197.	35.8	0.01584	0.208
CO_2	31.3	72.9	0.00428	0.45
C_2H_4	+10.	51.7	0.00569	0.21
O_2	−118.8	50.8	0.004042	0.604
N_2	−146.	35.	0.004603	0.37
H_2	−234.5	20.		

It will be noticed that the pressures needed to produce liquefaction are not large but that the temperatures to which some gases must be cooled are very low.

Liquefaction of Air. In 1895 Linde, in Germany, and Dewar and Hampson, in England, simultaneously developed machines which furnished liquid air in large quantities. These machines consist essentially of a compressor pump, an arrangement for removing all the moisture from the air to be liquefied (this is essential, as any moisture would solidify and stop up the tubes), and also a cylinder of lump sodium hydroxide to remove carbon dioxide. This latter arrangement is not essential, for stoppage by solid carbon dioxide seldom occurs and the solid carbon dioxide may be filtered out from the liquid air at the end of the process.

In the Linde machine the air is compressed to about 200 atmospheres, passed through a cylinder of calcium chloride to remove most of the moisture, and is given a preliminary cooling by passing through a coil of large diameter pipe immersed in a freezing mixture of crystalline calcium chloride and crushed ice. Almost all the remaining

* G. Teichner, *Annal. d. Physik.*, 13, 595–610 (1904).

moisture deposits as ice within this coil. The air then passes into a long spiral tube which is insulated from heat, and is allowed to expand through a valve down to a pressure of about 15 atmospheres. This expansion cools it a good deal. At the further end of the long insulated coil it expands through a second valve down to atmospheric pressure, and this expansion produces an additional cooling effect. Now, instead of escaping, the air which has been thus cooled is forced to travel backward to cool the oncoming air. This is accomplished by means of concentric tubes, a construction very similar to a Liebig condenser; that is, the tube through which the air comes from the pump is surrounded by a larger tube throughout its length, and the air which has passed through the expansions travels back through the outer tube. Thus the next lot of air expands from a lower temperature and we get an increase of cooling effect. This cooler air, traveling back, cools the oncoming air yet more, and by this self-intensification process the temperature is ultimately reduced to the point where the last expansion results in the liquefaction of a part of the air. The rest of the air, which does not liquefy, is nevertheless at the temperature of liquid air, and traveling back through the outside tube cools the oncoming air to such an extent that a still larger proportion liquefies in the final expansion.

Dewar Vacuum Jacketed Vessels. The liquid air is collected in Dewar vacuum jacketed vessels. Two flasks or test tubes are blown, one within the other, leaving a spherical or cylindrical space about one centimeter thick between them. This space is evacuated as perfectly as possible with the best mercury pumps, and is then sealed. A perfect vacuum is the best heat insulator known. These vessels are often silvered within the annular space before evacuation, in order that they may reflect radiant energy and thus further hinder the passage of heat through the vacuum jacket.

The Thomson-Joule Effect. The cooling effect produced by the expansion of a gas through a small aperture depends upon the variations from the gas laws. This is known as the Thomson-Joule effect.

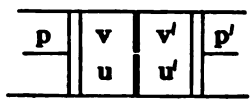


Fig. 32.

Suppose that we have a cylinder with two frictionless pistons and a partition containing a small aperture as shown in Fig. 32. Let p equal the pressure on the left-hand piston and p' equal the pressure on the right-hand piston. Let v equal the volume of the gas in the left-hand space, and v' equal the volume in the right-hand

space. Let U equal the internal energy of the gas in the left-hand space and U' equal the internal energy of the gas in the right-hand space.

Now, suppose the right-hand piston close against the partition, and exert a pressure on the left-hand piston driving all of the gas through the aperture. When this has been done, the left-hand piston will be against the diaphragm and the right-hand piston will have moved outward against the pressure p'. It is evident that pv = work done on the gas, and $p'v'$ = work done by the gas. Now if $pv = p'v'$ there is evidently no change in the internal energy of the gas, no change in temperature, and $U = U'$.

But suppose pv is less than $p'v'$; then the gas does more work than is done upon it. It can do this only at the expense of its own internal energy, its heat; therefore U' is less than U and we have a cooling effect.

Suppose pv to be greater than $p'v'$, then the gas will have a greater internal energy after having passed through the aperture than before. U' is greater than U, and the result of the expansion is a heating effect.

We may summarize these facts as follows: When $pv = p'v'$, *i.e.*, when the gas laws hold, $U = U'$ and there is no change in temperature. When $pv < p'v'$ the gas does more work than is done upon it, $U' < U$ and there is a cooling effect. When $pv > p'v'$ the gas does less work than is done upon it, $U' > U$ and there is a heating effect.

Application to Andrews' Isotherms. It will be remembered from Chapter XI that Andrews' isotherms are constructed by laying off values for the product pv on the vertical and values for p on the horizontal. If the gas laws formulated the behavior of gases we should so obtain straight horizontal lines. But the actual experimental values when plotted give us curves such as that in Fig. 33.

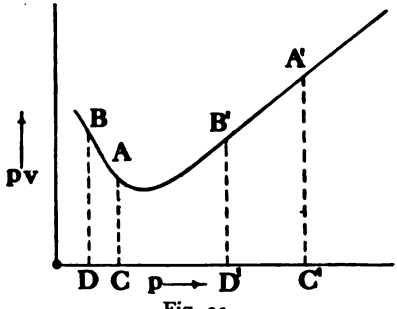


Fig. 33.

Suppose we have a gas under a pressure OC in Fig. 33, with the pv value represented by AC, and that we allow it to expand to the lower pressure OD when it shows the $p'v'$ value represented by BD. Evidently $pv < p'v'$ and this expansion must be accompanied by a cooling effect,

Suppose we have a gas under a pressure OC' with the pv value $A'C'$ and expand it to the pressure OD' and find its $p'v'$ value to be $B'D'$. In this case $pv > p'v'$ and this expansion must be accompanied by a heating effect.

If the Andrews' isotherm for the gas were a straight horizontal line, if the gas were ideal and its behavior corresponded exactly to the gas laws, pv would equal $p'v'$ and there could be neither heating nor cooling. It is thus clear that machines for the liquefaction of air, or other gases, will prove effective only if the gas shows deviations from the formulations of the gas laws.

The nearer gases are to their points of condensation the greater their divergences from the gas laws, therefore, the greater the effect of a given expansion. Thus a preliminary cooling given to the air before passing into the machine and undergoing the expansions is always a saving of labor and time.

At ordinary temperatures hydrogen varies from the gas laws in the sense of the ascending portion of Andrews' isotherm, indicated by the positions A' and B'. Thus hydrogen, compressed and sent through a liquid-air machine, instead of cooling itself will become gradually hotter, unless it is first cooled to a point where its deviations from the gas laws correspond to the conditions indicated by the positions A and B.

Uses for Liquid Air. Only one industrial application for liquid air has been found, the securing of oxygen from the atmosphere. Liquid nitrogen boils at about $-194°$ and liquid oxygen at about 10° higher. Therefore liquid air always contains a larger proportion of oxygen than the air from which it was made and, allowed to evaporate, the nitrogen vaporizes more rapidly than the oxygen. By subjecting liquid air to fractional distillation it is possible to obtain fairly pure oxygen. This method is a commercial success.

The most important uses for liquid air thus far are in scientific investigations when it is desired to secure the lowest possible temperature. With its aid, and the aid of machines constructed on the principle of the liquid-air machine, all known gases have been liquefied. Helium, the last to succumb to our efforts, was liquefied in 1908 by Kamerlingh Onnes.*

As a Refrigerant. As a refrigerant for ordinary purposes, it is not even so efficient as ice. The heat of vaporization of liquid air is about 50 cal. Raising one gram of gaseous air from its boiling point

* *Compt. Rend.*, 147, 421–424 (1908).

to 0° requires 18 cal., or a total cooling effect of 68 cals. is obtained from one gram of liquid air. The heat of fusion of ice is 79.2 cal. *i.e.*, for preserving perishable food products, cold storage, and the like, ordinary ice is more effective, weight for weight, than liquid air.

Motors. As a motive power it is in no sense different from compressed air. Owing to the expansions a compressed-air machine cools itself off and condensing the moisture in the atmosphere coats itself with ice, which may interfere with the moving parts.

Isothermal Compression. Thomas Andrews in 1869 first made clear the principles underlying the process of liquefaction.* Carbon dioxide was confined in a sealed tube over mercury; pressure could be increased at will and the apparatus was in a water bath maintained at a definite temperature. Holding the temperature constant at 13.1° he determined a series of pairs of values for p and v which, laid off on a coördinate system and joined, gave the curve marked 13.1° in Fig. 34. Changing the temperature of the bath to 21.5° and repeating, he obtained pairs of values which gave the isotherm marked 21.5° in the figure. In this same way he obtained all the isotherms shown and more.

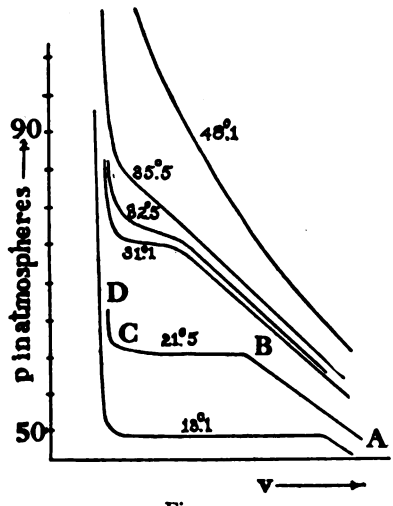


Fig. 34.

Consider the isotherm for 21.5°. At A we have a gas occupying a fairly large volume under a fairly low pressure. As the pressure increases the volume diminishes until point B is reached where a marked change in the behavior is observed. Attempts to increase the pressure fail, the volume diminishes while the pressure remains constant, as is shown by the horizontal part of the curve. Inspection of the contents of the tube shows that liquefaction begins at B and the diminution in volume corresponds to a diminution in the quantity of the gas and an increase in the quantity of the liquid. The pressure corresponding to this horizontal is the vapor pressure of liquid carbon

* *Phil. Trans. Roy. Soc.*, London, **159**, 575 (1869), and **166**, 421 (1876); *Phil Mag.* (5) **1**, 57 (1876).

dioxide at the temperature 21.5°. At *C* all the gas has been liquefied and from *C* to *D* large increase in the pressure produces but small decrease in the volume. The carbon dioxide shows the small compressibility of a liquid.

Isotherms at lower temperatures show longer horizontal stretches, at higher temperatures, shorter. The isotherm for 31.1° (or one a fraction of a degree above it) shows only a nick. The position of this nick gives, simultaneously, the critical temperature, pressure, and concentration. At temperatures above this there is no horizontal part at all and succeeding isotherms become more and more regular hyperbolas corresponding to Boyle's law which states that pv = a constant.

These horizontal stretches thus delimit the conditions within which we can have the substance CO_2 in the two phases, gaseous and liquid, in contact with each other. If we operate above 31.3°, it is impossible for us to have the two phases and we pass continuously from the gaseous to the liquid condition without the least indication of any abrupt change. These diagrams and considerations make clear, as nothing else can, the significance of the critical temperature, pressure, and volume (or concentration) of a substance.

Gibbs' Phase Law. The phenomena we have before us are some of many which are profitably formulated in what is known as Gibbs' phase law. This is more commonly called Gibbs' phase rule, but inasmuch as it formulates experimental facts, and all other such formulations are called laws, law is the better name for it. It is one of the six or eight greatest generalizations we have, and a potent aid in systematizing our subject and remembering facts. Its full significance can be appreciated only by applying it to case after case. We shall therefore state it now in order to be able to point out how it applies to numerous experimental facts described in this and succeeding chapters. But before we can state it we must define certain terms in the sense in which they are used in this formulation.

System. A system is any substance or group of substances which we may elect to study, considered as isolated from the surroundings. For instance, we may be investigating a gas in process of liquefaction, or some solid, a solution of that solid and the gas above it, or any other group of substances. It is convenient to refer to the whole group as " the system." By " isolated " we do not necessarily mean completely isolated, for we often consider that heat is given to the system or taken from it. Moreover, it is practically impossible to *completely* isolate any system.

Equilibrium. Processes, changes, occur within a system; more and more gas liquefies, more solid dissolves, etc. While this sort of change is going on the system is not in equilibrium. But if we determine just how much of each thing is there, then, after a time, again investigate and find none of our measured quantities have altered, we say the system is in equilibrium.

The kinetic pictures we shall later imagine as to the conditions of equilibrium are more or less theoretical, but by the word equilibrium we convey the simple straightforward fact that no quantity in the system alters with time.

Phase. Each different, homogeneous part of a system we call a phase. Thus the tube containing liquid and gaseous carbon dioxide, with which we illustrated the critical phenomena, contains a system of two phases, a liquid phase and a gaseous phase. The tube itself is not considered as part of the system. It is essential, truly, to isolate the system we wish to study from the surroundings, and it cannot be said not to take part in the processes involved in our study as it conveys the heat energy to or from the carbon dioxide, yet it might have been made of other material and the same changes could be brought about in the objects on which our attention is fixed, and therefore it is not included when we refer to this " system."

A solid in contact with a solution of itself and with the gas above consisting of some of the solvent and some of the solute, is a system of three phases, the solid, the solution, and the gas. Two liquids miscible to certain extents in each other, and the gas above them, consisting of the two solvents, is another system of three phases, two liquid phases and a gaseous phase.

We can never have more than one gaseous phase in a system, because all gases are mutually soluble in all proportions to form homogeneous mixtures. On the other hand, there is no limit to the number of different liquid or solid phases which we may have. These illustrations will suffice to indicate what we mean by the term phase and to enable anyone to count the phases in any system.

Homogeneous and Heterogeneous Equilibrium. When the equilibrium exists in one phase we call it homogeneous, when it exists between two or more phases we call it heterogeneous. In Chapter XII we learned how to calculate the degree of dissociation of gases. In all the cases there studied, for each temperature there is equilibrium between the not dissociated gas and the products of its dissociation. As all substances participating in the equilibrium are gaseous these

are all instances of homogeneous equilibrium. Equilibria with all the interacting substances in one liquid phase are also frequent and important. They too are homogeneous equilibria. The fundamental generalization for all cases of homogeneous equilibrium is the law of mass action and this is the subject of Chapter XXVI. The phase law tells us nothing whatever concerning homogeneous equilibrium, but it is the fundamental generalization for all cases of heterogeneous equilibrium and therefore we shall confine ourselves for the present to the latter.

Physical and Chemical Equilibria. We may also distinguish between physical and chemical equilibria, considering equilibria existing between conditions of aggregation, as between ice, water, and water vapor, as physical, and equilibria between substances and the products of their reaction as chemical.

Component. Sometimes a little difficulty is found in comprehending the exact import of the term component, and in differentiating between it and the term constituent. In the system which we were studying, and which introduced the subject of the phase law, we have liquid carbon dioxide in contact with gaseous carbon dioxide and in equilibrium. We have just one chemical individual, CO_2, and we say it is a system of one component. To be sure, CO_2 contains carbon and oxygen, but the proportions of carbon to oxygen are fixed (law of constant proportions), and we cannot alter one without altering the other. The elements here are not components, they are constituents. We might add some solid carbon or some gaseous oxygen to our system, but such additions would not in any wise alter the equilibrium we are considering, that between liquid and gaseous CO_2. Thus before a substance can be called a component it must take an active part in the establishment of the particular equilibrium in question.

There is yet another restriction to the term which we must understand before we can count the components in a system. Take the case described in Chapter XII. Solid NH_4Cl upon being heated dissociates to NH_3 and HCl. Evidently enough three different chemical individuals participate in this heterogeneous equilibrium, and one might jump at the conclusion that there are three components. This conclusion would be wrong. In the sense in which the word is used in the phase law this system contains, under some circumstances one, under other, two components. Suppose we heat some solid NH_4Cl in a closed tube containing nothing else. A part

will become gaseous and a part of this will dissociate to equivalent quantities of NH_3 and HCl. At any definite temperature this will proceed until a definite gaseous pressure is produced and then equilibrium is reached. Now this equilibrium is like that in the system consisting of liquid and gaseous CO_2. If we raise the temperature, more solid NH_4Cl will vaporize, dissociate, and increase the gaseous pressure, or more liquid CO_2 will vaporize and increase the gaseous pressure. Simultaneously the concentrations of the gases increase. Upon lowering the temperature the reverse phenomenon occurs in both cases. NH_3 and HCl appear and disappear in equivalent quantities as if NH_4Cl vaporized and sublimed as a whole without dissociation. Therefore this system is to be considered as of one component.

But if we add NH_3 or HCl, either one of the products of the dissociation, to the system, they are no longer present in equivalent quantities. Suppose we add some NH_3 and then lower the temperature a little. Solid NH_4Cl will form as before. This removes NH_3 and HCl in equivalent quantities from the gaseous phase and alters the ratio between the concentrations of gaseous NH_3 and HCl. For each temperature now there is a definite concentration of NH_3 and a definite and different concentration of HCl. In other words, to define the equilibrium conditions we must give the quantities (concentrations) of *two* chemical individuals. Acting upon this idea we say, as components we shall consider only those chemical individuals whose concentrations must be stated in order to define the conditions of equilibrium.

And still we have not finished with this rather troublesome definition. It might appear from the foregoing that NH_3 and HCl were necessarily the two components of the system. But in such cases, where we have interaction between three substances it is always the fact that fixing the concentration of two arbitrarily, the concentration of the third fixes itself automatically. Now then it matters not at all which two we fix, and so, if we call them *A*, *B*, and *C*, we may say the two components are *A* and *B*, *A* and *C*, or *B* and *C*. Naturally we always choose those two most conveniently determined analytically.

To sum up: The number of components of a system is the smallest number of chemically individual substances, of independently variable concentrations, the concentrations of which must be defined to define the conditions of equilibrium. Of course there is no limit to the number of components which we might have in some one system.

"Order" of Equilibrium. If the system in equilibrium contains one component we say it is an equilibrium of the first order, if it contains two components we say it is an equilibrium of the second order, etc.

Degrees of Freedom. No matter what the system we may have under consideration, there are only three conditions which we know how to alter, namely, the temperature, the pressure, and the concentration. These are then three variables, and if we find we can alter any one of these, but one only, we say we have one degree of freedom; if we can alter two independently we have two degrees of freedom; if we can alter three we have three degrees of freedom. It is possible to have more than one variable concentration in one system and hence we may have more than three degrees of freedom.

Application to Isothermal Liquefaction. The significance of "degrees of freedom" is easily comprehended by applying the idea to the process we have under consideration, the liquefaction of a gas.

Suppose we have an apparatus as used by Andrews and at the beginning we have only gaseous CO_2 enclosed over mercury in the sealed tube. We may make the temperature high or low through a definite range and may also make the pressure what we like between certain limits. Having made both temperature and pressure conform to our will, the third variable, the concentration, however, is fixed. We cannot simultaneously arrange the concentration arbitrarily. We may choose a definite temperature and a definite concentration, but if we do so, we find the pressure is automatically fixed for us. We may choose a definite pressure and concentration, but we can realize them only at one definite temperature. We have, as it were, two wishes which we may distribute as we like among the three variables; but we cannot have three wishes. In the phraseology of the phase rule we have two degrees of freedom, and our system contains one component and one phase.

With this same apparatus let us choose some definite temperature, say 21.5°, thus using up one of our degrees of freedom, and then increase the pressure. We thus use our second degree of freedom and the concentration (volume) takes on automatically corresponding values. Increasing the pressure we shall presently reach the point (*B* in Fig. 34) where liquefaction begins. We now have a system of one component and two phases, and, curiously enough, so long as we choose to hold the temperature constant we cannot alter the pressure, nor the concentration of either phase. Efforts to increase

the pressure liquefy more and more gas until all is liquid, but do not alter the pressure. Efforts to diminish the pressure cause more and more liquid to evaporate until no more is left. In either case, one phase disappears entirely before we can produce any change in the pressure.

Evidently if we have a system with one component and two phases, we can choose a value for only one of the variables. We have but one degree of freedom of choice. This is true without exception for all pure substances, so we can make a broad generalization as follows:

In systems of one component the number of phases plus the degrees of freedom is always equal to three.

This is the simplest case of the many which are included in the general statement of Gibbs' phase law. As we bring up other experimental facts we shall develop this law to its most general expression, which is: If C equals the number of components, $C + 2$ is the maximum number of phases possible. If P is the number of phases, and F the number of degrees of freedom, $C + 2 - P = F$.

Supercooling. If we have a gas (vapor) at pressure temperature and concentration such that a small lowering of the temperature should produce liquefaction we may, under some circumstances, cool and yet not observe liquefaction. We have already spoken of this fact in the chapter on radioactivity. Saturated water vapor may be cooled by a sudden expansion and yet no mist forms unless dust particles or charged ions are present to act as nuclei. We say the substance is in a supercooled condition. Infracooling would be a more logical term than supercooling.

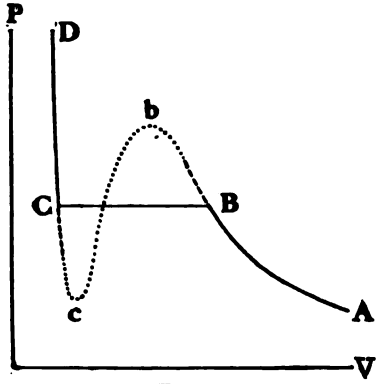


Fig. 35.

Figure 35 is a reproduction of the isotherm for CO_2 at 21.5° and the condition of a supercooled gas, which should be liquefying but is not, is represented by positions on the broken line portion of the curve above B and below b.

Stable and Metastable Equilibrium. A very small thing will upset the conditions; particles of dust, or charged ions, or best and surest of all, particles of the same substance as a liquid, the other

phase, start condensation which proceeds until the conditions are readjusted and they are represented by some position on the full line of the isotherm. We distinguish then between conditions of what we call stable equilibrium, all of which are represented by the full line of the isotherm, and these others which we can realize, but which a small thing will upset, and which we call metastable equilibria.

There is no contradiction to Gibbs' phase law in these phenomena. When we have a supercooled gas there is but one phase present, not two. The introduction of mere traces of the other phase at once starts a change which does not stop until conditions of stable equilibrium are reached.

Dew. We have many examples of this phenomenon on a large scale. For instance, during a hot summer day much water evaporates and is held in the atmosphere as water vapor. In the evening, the temperature falls and the air is apt to become supersaturated with water vapor and the moisture precipitates where there is some moisture already, that is, on the surface of the ground and on vegetation, as dew. Moreover, these objects radiate heat into space and so cool off more rapidly than the air above them; this, of course, increases the deposition of dew. Clouds hinder radiation into space and less dew deposits on cloudy than on clear nights.

Formation of Clouds. Again, after a hot and windless day, dust has settled; it may grow cooler and a supercooled condition may exist at an elevation. If we watch for it, we may frequently see a small cloud grow to many times its size. It is surprising how few appear to have observed this common phenomenon. It sometimes happens that the atmosphere becomes so supersaturated that clouds form with extreme rapidity, and we get heavy showers, occasionally what we describe as a cloud-burst.

Superheating. On the other hand, we know that water in a perfectly clean flask may be heated above its boiling point. This is only too readily shown, especially when we try to boil solutions of the alkalies which clean a flask or beaker of all grease. The liquid superheats and then, suddenly, a volume of vapor forms which throws out part of the contents. The liquid "bumps." Globules of water suspended in oil of the same specific gravity have been heated to 145°.

The conditions of superheated liquids are represented by positions on the prolongation of the curve *DC* below *C* and above *c*. These are likewise conditions of metastable equilibrium, but one phase is present where there should be two and the phase law does not apply.

Small things upset the metastable equilibrium. The presence of the least particle of the vapor prevents such superheating.

Glass beads, platinum scrap, bits of porcelain, sharp edges of almost any sort diminish bumping because they appear to facilitate the formation of the first bubble of vapor. Porous substances such as pumice, even capillary tubes full of air, act in the same way.

Prolongations of the Isotherm. We can then realize conditions represented by a prolongation of the isotherm AB beyond B in the direction of b and by a prolongation of DC beyond C in the direction of c. All conditions for stable equilibrium are represented by positions on the full lines joining A, B, C, and D.

There appear to be limits to our ability to proceed along the parts Cc and Bb. If we overstep these limits, even though no particle of the second phase has been introduced, it will form and then of course the system will readjust itself to the stable state.

Application of van der Waals' Equation. It is exceptionally interesting that we can derive these prolongations from van der Waals' equation. Multiplying both sides of the equation $\left(p+\frac{a}{v^2}\right)(v-b)=RT$ by v^2 we obtain, $(pv^2+a)(v-b)=RTv^2$. Multiplying out and arranging we obtain $v^3-\left(b+\frac{RT}{p}\right)v^2+\frac{a}{p}v-\frac{ab}{p}=0$. This is an equation of the third order and so for a definite temperature and pressure there are three values for v. Inserting values for T and p and solving for the values of v we obtain the sinuous curve shown in Fig. 35, wherein the portion so calculated but not realized is indicated by dots, not dashes.

Labile State. It will be noticed that on this theoretical isotherm we have a part, from c, the lowest point, to b, the highest, where increase in pressure appears to be accompanied by an increase in volume, a wholly unrealizable state of affairs. This is sometimes called the labile state.

"Complete" Equilibrium. There is another feature of the conditions here represented to which attention must be called. Along the horizontal, from B to C, we may have a series of different volumes at one temperature and one pressure. But the concentrations of the phases remain the same even though the volume is altered. We cannot alter one of the variables (pressure, temperature, concentration) without causing the total disappearance of one phase. A slight increase in pressure, maintained, will liquefy all the gas; a

slight decrease in pressure, maintained, will vaporize all the liquid. When the conditions are these the system is said to be in " complete " heterogeneous equilibrium.

Mobile Equilibrium. In another class of systems a change in one variable does not cause the disappearance of a phase but only a corresponding change in another variable, the concentration. It will be well to give an illustration though properly its consideration comes later. Suppose we have a solution in equilibrium with gaseous solvent above it. The gaseous pressure is the vapor pressure of the solution at that temperature. Holding the temperature constant let us diminish the pressure. Some solvent will evaporate, but this increases the concentration of the solution. The more concentrated the solution the less its vapor pressure, so we shall soon have equilibrium again but with a lower pressure and different concentrations in two phases. Holding the temperature constant let us increase the pressure. Some solvent will condense. This diminishes the concentration of the solution and increases its vapor pressure, and soon we have equilibrium again, but this time with a higher pressure. This system is said to be in mobile equilibrium. The fundamental difference between " complete " and " mobile " equilibrium is sufficiently apparent.

An old mechanical analogy is helpful in fixing these terms in mind. A cone standing on its base is in stable equilibrium. If a force is applied in such a way as to tilt it slightly it will resume its original position as soon as the force is removed. A cone on its side may be likened to a system in mobile equilibrium. We may roll it to a new position and it will remain there with no tendency to resume its original position. A cone balanced on its apex is in metastable equilibrium. Under exceptional conditions we can have the cone remaining in this position indefinitely, but a very small thing will upset it and it will fall until it reaches a position of stable or mobile equilibrium. A cone supported by its apex alone and at a slant is in the act of falling; it is in a labile state. We cannot produce this condition in such a way as to hold it even for a short interval of time. It may be considered as the condition, or conditions, through which a system may pass while undergoing a change.*

Calculation of the Critical Constants. The higher the temperature at which the isotherm is determined the shorter the horizontal *BC* and the flatter the sinuosities, until, at the critical temperature

* The term labile is sometimes used as if it were synonymous with metastable.

there is no horizontal line, but merely a nick; call it a point. Then at this temperature the three values calculable for v become the same. Here then the three roots of the equation on page 270 become identical, and this root must be v_c, the critical volume. Rewrite the equation indicating $\left(b + \frac{RT}{p}\right)$ by q, $\frac{a}{p}$ by r, and $\frac{ab}{p}$ by s, and we have, $v^3 - qv^2 + rv - s = 0$. The theory of equations tells us that in an equation of this form when the three roots are the same, v_c, that $v_c = \frac{q}{3}$, $v_c^2 = \frac{r}{3}$, $v_c^3 = s$. Then $3\,v_c = b + \frac{RT}{p}$; $3\,v_c^2 = \frac{a}{p}$; $v_c^3 = \frac{ab}{p}$. For these conditions we have the critical pressure p_c and the critical temperature T_c. Combining the second and third of our expressions we find $v_c = 3\,b$. Substituting this value in the second we find $p_c = \frac{a}{27\,b^2}$. Substituting these two values in the first equation we find $T_c = \frac{8\,a}{27\,bR}$, and thus we have the critical constants expressed in terms of van der Waals' corrections to the gas laws. By this means we may calculate the values of a and b for any substance from a knowledge of its critical constants or, conversely, we may calculate the critical constants from a knowledge of the values of a and b.

Law of Corresponding Conditions. A very remarkable deduction may be made from van der Waals' equation. Instead of expressing the values for p, v, and T in the usual units let us express them all as fractions of the critical values of these quantities. Let $r = \frac{p}{p_c}$; then $p = rp_c$; let $n = \frac{v}{v_c}$, then $v = nv_c$; let $m = \frac{T}{T_c}$, then $T = mT_c$. Substitute these values in van der Waals' equation. We then have $\left(rp_c + \frac{a}{(nv_c)^2}\right)(nv_c - b) = RmT_c$. Now in this equation substitute the values we have just found for the critical constants, $3\,b$ for v_c, $\frac{a}{27\,b^2}$ for p_c and $\frac{8\,a}{27\,Rb}$ for T_c and we discover the extraordinary fact that terms cancel until the equation takes on the very simple form, $\left(r + \frac{3}{n^2}\right)(3\,n - 1) = 8\,m$. Not a quantity remains which is peculiar to, or characteristic of, any one substance; a and b and even the gas constant have disappeared. We have only fractions

of the critical conditions expressing their interrelationships, and this equation ought to hold for any and all substances.

Reduced Equation of Conditions. This is called the "reduced equation of conditions," and it tells us that we should compare substances when their pressures, etc., are the same fractions of the critical constants of the several substances. It makes clear that the critical constants are most fundamental and characteristic values.

This reduced equation tells us that whatever particular value we find for a particular substance under definite conditions, we ought to find the same value for that property for any other substance, provided we investigate it under the same conditions with relation to its critical constants. For instance, all liquids should have the same vapor pressures at temperatures which are the same fractions of the critical temperatures. We have already had occasion to allude to one instance of this in connection with our comparisons of molecular volumes, and there stated that these volumes were appropriately compared at the boiling points because these, on the absolute scale, are close to two-thirds of the critical temperatures.

Like so many of these eminently simple and obvious conclusions reached by mathematical or thermodynamical processes it does not accurately formulate the facts. It represents an ideal and not the real, experimentally found relationships, just as the simple gas laws do not formulate the actual behavior of any known gas. This must not be taken to indicate that there is anything the matter with our mathematics, but rather that there is some error or omission in our premises. All such results are just as accurate as the premises but not more so. The premises are the result of actual laboratory experiment and are thus, from all points of view, of the greatest importance. One experiences such a feeling of satisfaction upon completing a deduction of this sort that it is but natural to exaggerate what has been accomplished, and there is therefore a tendency to get farther and farther away from the fundamental experimental facts which must be won at such an expenditure of time and labor in the laboratory, and to indulge in longer and longer mathematical flights, for which less patient plodding is needed. These flights sometimes lead to formulæ which, as Armstrong puts it, are raised to the nth power of improbability. While this remark does not apply to the equation just derived, it will not be amiss to plead in favor of remaining within communicating distance of the objective universe while we disport in the subjective.

CHAPTER XXI

VAPOR PRESSURE

WHEN we have a liquid or a solid in a closed vessel, a portion of it becomes vapor and, as such, exerts a pressure like all gases. This gaseous pressure reaches a maximum for a definite temperature, and this maximum is the vapor pressure of that liquid at that temperature. We may consider vapor pressure as the measure of the tendency of the substance to become a gas.

Many solids, of course, at ordinary temperatures, do not give enough vapor for us to measure the resulting gaseous pressures. Yet we consider all substances as, theoretically at least, having vapor pressures. This is not so severe a stretch of the imagination as it might at first appear to be. A number of metals, just after being vigorously rubbed, have distinctly perceptible odors. What else can cause this but traces of the metal as a vapor?*

Measurement of Vapor Pressure. There are two methods of measuring vapor pressure, the static and the dynamic. We shall first consider the static method.

Static Method. The following is an easily carried out and instructive experiment. Four barometer tubes are inverted over mercury. By means of pipettes with their ends curved upward, insert a small quantity of water in one, of alcohol in the next, and of ether in the next. Leave the fourth with no addition as a measure of the barometric pressure. The mercury falls a few millimeters in the tube in which water was put, considerably more in that in which alcohol was put, and most in that in which ether was put. Vapor pressures of different substances are thus shown to be different. The fall of the mercury is evidently a direct measure of the gaseous pressure produced by the vapor of the substance in the space which was originally a Torricellian vacuum.

Effect of Temperature. Raise the temperature by surrounding the tubes with jackets of a heating liquid or gas. The mercury falls,

* Vapor tension is a term sometimes used instead of vapor pressure. But vapor pressure is to be preferred inasmuch as the measure is of a gaseous pressure. Vapor tension reminds one of surface tension, a wholly different quantity, and might lead to confusion. Moreover, we do not need two names for one thing.

that is, the vapor pressure increases with the temperature. This is an invariable rule, no exceptions are known. Following is a table of the vapor pressures of these substances (and of ice) at different temperatures.

VAPOR PRESSURES IN mm. OF MERCURY

Temperature.	Water.	Ice.	Alcohol.	Ether.
−50	.....	0.034	.....	.....
−40	.....	0.105	.....	.....
−30	.....	0.292	.....	.....
−20	0.960	0.787	3.34	62.99
−15	1.451	1.257	.....	.....
−10	2.159	1.974	6.47	111.81
−5	3.167	3.032	.....	.....
0	4.579	4.579	12.24	184.9
+5	6.528	.....	.....	.....
10	9.179	.....	23.77	291.78
15	12.728	.....	.....	.....
20	17.406	.....	44.00	442.36
25	23.546	.....	.....	.....
30	31.555	.....	78.06	647.92
35	41.853	.....	.....	.....
40	54.97	.....	133.42	921.18
45	71.50	.....	.....	.....
50	92.17	.....	219.82	1 276.11
55	117.77	.....	.....	.....
60	149.21	.....	350.2	1 728.13
65	187.51	.....	.....	.....
70	233.79	.....	540.9	2 293.91
75	289.32	.....	.....	.....
80	355.47	.....	811.8	2 991.40
85	433.79	.....	.....	.....
90	526.00	.....	1 186.5	3 839.71
95	634.01	.....	.....	.....
100	760.00	.....	1 692.3	4 859.01
110	1 075.4	.....	2 359.8	6 070.38
120	1 491	.....	3 223	7 495.73
130	2 030	.....	4 320	9 157.42
140	2 718	.....	5 666	11 078.2
150	3 581	.....	7 326	13 281.0
160	4 651	.....	9 366	15 788.1
170	5 961	.....	11 856	18 622.2
180	7 546	.....	14 763	21 804.3
190	9 442	.....	18 178	25 355.1
197	.....	.....	.....	27 208
200	11 688	.....	22 164	.....
210	14 324	.....	26 821	.....
220	17 389	.....	32 097	.....
230	20 925	.....	38 176	.....
243.6	.....	.....	47 698	.....
364.3	147 898	.....	.....	.....

Vapor Pressure Curves. If we plot these pairs of values on a coördinate system, laying off temperatures on the horizontal and

vapor pressures on the vertical, we obtain what are called vapor pressure curves with which we shall have much to do. The range in the table is so enormous it is impossible to plot the values to scale in a figure of reasonable size. Figure 36 contains a few sections of these curves. Since, at the critical temperature and pressure, gas and liquid

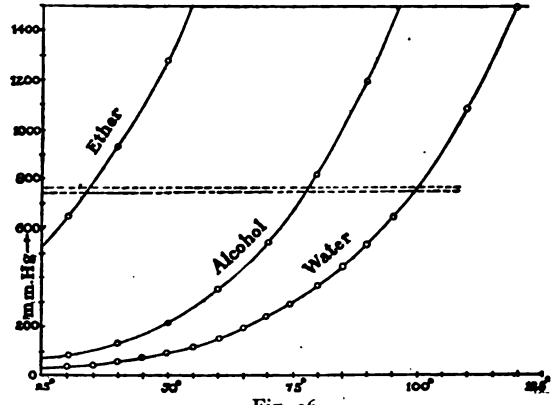


Fig. 36.

become identical, all vapor pressure curves must end abruptly at these points.

Quantity of Substance. Add more of the substance to one of the tubes. No alteration in the mercury level is produced excepting that to be expected from the additional weight resting on the mercury surface. The vapor pressure is independent of the quantity of liquid present.

Presence of Another Gas. If the tubes had contained air or some indifferent gas and the mercury had not stood at the barometric height to begin with, upon adding one of the liquids the drop of the mercury would nevertheless have been exactly the same. In other words, the vapor pressure of a substance is independent of whatever else may or may not be present in the gaseous phase. The total pressure is the sum of the partial pressures, a statement we made as fundamental for solutions of gases in gases. If we add a substance which dissolves in the liquid already there, we obtain the vapor pressure of the solution, a subject of such importance we shall consider it separately.

Application of the Phase Law. With the two phases in contact with each other and in equilibrium, we are on the horizontal line of an isotherm like those in Fig. 34. Imagine one of our barometer tubes prolonged upward and closed by a movable but strictly gas-

tight piston. Holding the temperature constant, pull up this piston, thereby increasing the volume of the gaseous phase. The mercury will not change its level, but more substance will evaporate to fill the increased volume with gas of exactly the same concentration as at first. The level of the mercury will not alter till the last particle of the liquid phase has disappeared. Push the piston down, thereby diminishing the gaseous volume. The mercury level is not thereby lowered. More and more gas liquefies, so maintaining the concentration of the gaseous phase unaltered and the mercury remains stationary until the last particle of gas has liquefied and the piston rests directly on the liquid.* These facts are repetitions of what we have studied in Chapter XX, but they are fundamentally important and must be thoroughly learned. We have a system of one component and two phases in complete heterogeneous equilibrium, and the phase law tells us we have then only one degree of freedom. This we exhausted when we chose a definite temperature for the experiment and so we can change neither the pressure of the system nor the concentrations of the phases.

Application of the Kinetic Theory. We assume a gas consists of molecules flying about with great velocities. Then in the gaseous phase of the system under consideration, some molecules undoubtedly get within the sphere of attraction of the liquid molecules while traveling so slowly they have not kinetic energy enough to get away again, but are retained. In other words, liquefaction is undoubtedly proceeding all the time. But on the other hand we think of the liquid molecules as moving with notable velocities also, and must imagine that some reach the surface with enough kinetic energy to pass through and to fly off into the gaseous phase. This is our plausible explanation of the existence of vapor pressures.

Balanced Action. Thus, as we picture the mechanism of equilibrium, it is anything but a condition of rest, rather is it one of restless activity. That we note no change we believe to be due to the fact that as many molecules enter the liquid phase as leave it per unit time. We call this " balanced action."

Formulation. Let C_1 equal the concentration of the gas and C_2 the concentration of the liquid, in any convenient units, grams, or molecular weights per cm^3, or per liter. Then, if the temperature is

* In these statements temporary fluctuations of the mercury level are disregarded because they are due solely to the fact that such systems require a little time to reach equilibrium.

constant, $\frac{C_1}{C_2}$ = a constant. This is a formulation of experimental facts and there is nothing theoretical about it. It is also a simple application of the law of mass action, to be considered in detail in Chapter XXV. While, as has been said, this law is our great generalization for all cases of homogeneous equilibrium, we see from this instance that it is applicable also to heterogeneous equilibria.

Evaporation. As is well known, evaporation of a liquid is accompanied by a cooling of the liquid. Put a watch glass in a pool of water on a block of wood. Put in the watch glass a little ether, or carbon disulphide, or any other liquid which has a high vapor pressure at low temperatures, and hasten the evaporation by keeping down the concentration of the gaseous phase by fanning or blowing across the surface. The cooling effect is sufficient to freeze the water. According to our kinetic theory it must be the molecules with the greatest velocities which leave the liquid to enter the gaseous phase. According to our theory that heat is a mode of molecular motion these must be the warmest molecules. The slowest, coldest molecules must be left behind, and so we have a plausible explanation for the observed facts.

Heat of Vaporization. A substance evaporates at all temperatures, even the lowest, but since, without exception, vapor pressures are greater the higher the temperature, evaporation may be hastened without limit by heating. The heat given to the system disappears as such and in its place we have a gas where we had a liquid or solid. Upon liquefaction of the gas exactly the same amount of heat which so disappeared reappears. On this account it is sometimes said to have been rendered latent and "latent heat of vaporization," "latent heat of fusion," are familiar terms. But this term "latent" is undesirable, for there is conversion of one form of energy into an equivalent quantity of another form in this process. Heat is converted into volume energy when a liquid becomes a gas and volume energy is converted to heat when the gas liquefies. Solid and liquid are distinctly different things with whole sets of widely different properties. Liquid is solid plus energy and this energy makes the two things more different than, for instance, copper and silver. When, by heat, we cause PCl_5 to dissociate into PCl_3 and Cl_2 we say the heat is absorbed, converted to chemical energy, seldom do we say it is rendered latent. It is desirable to drop this word latent, tending as it does to obscure the analogy which actually exists between changes in conditions of

aggregation and chemical reactions. These changes in conditions of aggregation are, in fact, our simplest chemical reactions.

By heat of vaporization we mean the number of calories required to convert one gram of a liquid to a gas.

Molecular Heat of Vaporization. By molecular heat of vaporization we mean the number of calories required to convert a molecular weight in grams of a liquid to a gas.*

The heat of vaporization for any substance is less the higher the temperature until, at the critical temperature, it equals zero, for, at this temperature, there is no difference between the conditions of aggregation. This is shown by the following values for the heats of vaporization of one gram of liquid carbon dioxide at different temperatures.

Temperature	−25°	0°	22°	30.0°	30.8°
Calories	72.23	57.48	31.8	11.60	3.72

Boiling Point. If we had increased the temperature in one of our barometer tubes sufficiently, we should have driven the mercury inside down to the same level as the mercury in the trough outside. Then the vapor pressure of the substance would evidently have been the same as the atmospheric pressure. At this temperature the tendency of the substance to become a vapor just balances the pressure of the atmosphere. It is at its boiling point.

Ebullition. When a liquid is heated in an open vessel the atmospheric pressure holds it down, as it were, to its proper volume. But when the vapor pressure reaches a value equal to this pressure upon it, bubbles of the substance as a vapor form within the body of the liquid. We then have the phenomenon of ebullition; we say the substance is boiling. It is evident that if the tendency to become vapor is less than the pressure upon the surface of the liquid, bubbles of vapor cannot form in the interior, the boiling point has

* The following are a few values for heats of vaporization. The second column contains the number of calories required to convert one gram of the liquid to a gas; the third contains this quantity multiplied by the molecular weight, giving the molecular heats of vaporization.

	1 g.	Mg.
Water, 0°	589.5	10 611
Water, 100°	535.9	9 700
Ammonia, 16°	297.4	5 100
Sulphur dioxide, 0°	91.2	5 900
Ethyl alcohol, 0°	236.5	10 900
Ethyl alcohol, 78°	206.4	9 500

not been reached. Hence the definition for boiling point is the lowest temperature at which bubbles of vapor can form within the body of the liquid. It is clear that any one substance may have an infinite number of different boiling points, each corresponding to a different external pressure. By the term "boiling point" as ordinarily used, without qualification, we mean the temperature at which the substance has a vapor pressure equal to the normal atmospheric pressure (760 mm.).

Graphical Representation of Boiling Points. In Fig. 36 follow the horizontal corresponding to a vapor pressure of 760 mm. It cuts the ether curve at 34.6°, the alcohol curve at 78.3°, the water curve at 100°, and these are the "boiling points" of these substances. But suppose the atmospheric pressure happens to be 740 mm. when we undertake to determine these boiling points; not at all an unusual circumstance. Follow the horizontal corresponding to a vapor pressure of 740 mm. It cuts the ether curve at 33.8°, the alcohol curve at 77.6°, and the water curve at 99.2°, and these are the temperatures at which ebullition will occur. Our results will all be too low. Neglect of the correction so obviously necessary is one of the reasons for the divergent values we often find in the literature.

If the pressure were 1000 mm. we can see from the figure that ebullition would occur in ether at 42.5°, in alcohol at 85°, and in water at 108°. Under the high pressures in a steam boiler water is not necessarily boiling though it may be far above its "boiling point." If the pressure in a boiler is 150 pounds per square inch, the water is boiling at about 180°. This explains the severity of scalds from bursting boilers.

Constancy of Boiling Point of a Pure Substance. For any pure substance there is then a definite vapor pressure for each temperature. By no means can we raise the temperature without simultaneously raising the vapor pressure. It follows that if we hold the pressure constant we cannot heat a liquid above a definite corresponding temperature. Heating a liquid in an open vessel the pressure upon it is the atmospheric pressure and this is practically constant. When the temperature has gone up until the vapor pressure of the liquid equals this atmospheric pressure, ebullition begins and though we continue to heat, the temperature rises no further. If we apply two burners where we had one we hasten the rate of vaporization, the violence of the ebullition, but we do not and cannot increase the temperature which remains constant until all the liquid

has boiled away. It is because of this fact that the boiling point of a substance under a definite pressure is so characteristic a constant for a pure substance and so frequently used as a means of identification.

This is one of the many facts included in the phase law. We have a system of one component and two phases and since $C + 2 - P = F$ we have $F = 1 + 2 - 2 = 1$, or one degree of freedom. We chose atmospheric pressure, whereupon the other variables, concentration and temperature, became automatically fixed.

The Dynamic Method of Measuring Vapor Pressure. We can arrange an apparatus to maintain pressure constant at any desired value from a few millimeters upward. Putting a liquid in this apparatus we can determine the temperature at which ebullition begins. In this way, called the dynamic method, we again obtain a series of pairs of values which we can plot and obtain, of course, the same curves shown in Fig. 36. This dynamic method is to be preferred to the static method first described, as by it we can make accurate determinations more easily.

Determination of the Boiling Point. In determining boiling points the thermometer is inserted in the vapor, and not in the liquid, for the temperature of the latter is more likely to oscillate because it is being directly heated and temporary conditions of superheating may intervene.

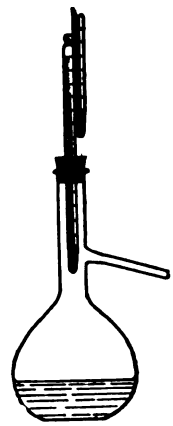


Fig. 37.

Correction for Mercury not in Vapor. All the mercury should be in the vapor, but usually some protrudes and is consequently at a lower temperature. Moreover, glass expands as well as mercury; therefore what we observe is not the true expansion of mercury but an apparent expansion, because mercury expands more rapidly than the glass container. The apparent (observed) expansion is the difference between the two, and its coefficient is 0.000 158 of the volume per degree for Jena glass.

By means of a second thermometer, placed as shown in Fig. 37, determine the average temperature of the protruding thread. Call this t_2. Let the temperature which is read on the thermometer with its bulb in the vapor be t_1. Let n equal the length in degrees of the protruding thread. The length is a measure of the volume of mercury if the capillary is of even diameter. This length is, then, too short by $n\,(t_1 - t_2)$ 0.000 158,

and the true boiling point is given by the formula

$$t_1 + n\,(t_1 - t_2)\ 0.000\ 158.$$

This correction is by no means negligible. For instance, aniline boils at about 180°. Suppose that 100° of the mercury thread projects and that its average temperature is 30°. Substituting these values in the above formula we get $100\,(180 - 30)\ 0.000\ 158 = 2.31°$ as the correction which should be applied. Without this correction our observation is no less than 2.31° too low.

It is convenient to have a set of short thermometers which may be wholly immersed in the vapor, each one covering an interval of about 50°. These eliminate the above correction but they do not eliminate the pressure correction.

Regularities in Boiling Points. Many investigations have been devoted to discovering regularities in the boiling points and have resulted in a number of rules, each applicable only within a relatively small group of substances. For instance, H. Kopp in 1842 compared the boiling points of numerous organic substances at 760 mm. pressure. He found:

1. With analogous substances the same change in chemical composition gives about the same change in the boiling point.

Acids:

Formic.	Acetic.	Propionic	n-Butyric.	n-Valeric.	n-Caproic.
$HCOOH$	CH_3COOH	C_2H_5COOH	C_3H_7COOH	C_4H_9COOH	$C_5H_{11}COOH$
99.9°	119°	141°	163°	185°	205°
Difference in boiling points:	19°	22°	22°	22°	20°

Alcohols:

Methyl.	Ethyl.	n-Propyl.	n-Butyl.	n-Amyl.
CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH	$C_5H_{11}OH$
66°	78°	97°	117°	137°
Difference in boiling points:	12°	19°	20°	20°

2. The boiling points of isomeric (metameric) substances of analogous constitution are nearly the same.

$C_6H_{12}O_2$	butyl acetate $CH_3COO \cdot CH_2CH_2CH_2CH_3$	124°
	propyl propionate $CH_3CH_2COO \cdot CH_2CH_2CH_3$	122°
	ethyl butyrate $CH_3CH_2CH_2COO \cdot CH_2CH_3$	121°

3. Isomeric (metameric) substances which are distinctly dissimilar in constitution often have widely different boiling points.

$C_3H_6O_2$	propionic acid CH_3CH_2COOH	141°
	methyl acetate CH_3COOCH_3	57°

4. CH_2 added in the side chain of aromatic hydrocarbons increases the boiling point a little more than the average of 20°, but in the ring itself it increases the boiling point about 30°.

	Boiling point.			Boiling point.	
Benzene, C_6H_6	80.5°	30.5°	Toluene, $C_6H_5CH_3$	111°	23°
Toluene, $C_6H_5CH_3$	111°	31°	Ethyl benzene, $C_6H_5C_2H_5$	134°	23°
Orthoxylene, $C_6H_4(CH_3)_2$	142°		Propyl benzene, $C_6H_5C_3H_7$	157°	

Boiling Point not Exclusively Additive. Attempts to prove the boiling point to be an additive property have failed. When CH_2 was found to make the same difference in so many cases, the hope was entertained that we might ascribe a certain effect for each atom present and so calculate the boiling point as the sum of these, much as we calculate molecular refractions as the sum of the atomic refractions. That this is clearly impossible appears from the single example of the isomeric but dissimilarly constituted substances, propionic acid and methyl acetate. While undoubtedly in a measure additive, the boiling point is then also a constitutive property.*

Boiling Point and Critical Temperature. Guldberg † and Guye ‡ showed that the boiling point on the absolute scale, T_b, is about two-thirds of the critical temperature, T_c.

	T_b	T_c	$\frac{T_b}{T_c}$
Oxygen	90	155	0.58
Chlorine	240	414	0.58
Sulphur dioxide	263	429	0.61
Ethyl ether	308	467	0.66
Ethyl alcohol	351	516	0.68
Benzene	353	562	0.63
Water	373	637	0.59
Phenol	454	691	0.66

Trouton's Law. According to the above table, substances at their boiling points are at temperatures the same fractions of their critical temperatures. According to the "reduced equation of con-

* S. Young, *Phil. Mag.*, 9, 6 (1905), found that for many substances the increase (Δ) in the boiling point produced by substituting CH_3 for H was a function of the boiling point (T) of the substance on the absolute scale, expressible in the formula:

$$\Delta = \frac{144.86}{T\,0.0148\sqrt{T}}.$$

† *Zeitschr. f. phys. Chem.*, 5, 376 (1890).

‡ *Bull. Soc. Chimique* (3), 4, 262 (1890).

ditions " all properties should here be comparable. It has been found that the molecular heat of vaporization of a substance at its boiling point is between 20 and 25 times the boiling point on the absolute scale. This is known as Trouton's law. The boiling point of water is 373°. Multiplying this by 25 we obtain 9325. The molecular heat of vaporization of water at its boiling point is 9700. Better correspondence than this is shown by other substances, but it should be understood that this " law " is a rather rough approximation.

Melting Point. If we slowly raise the temperature of a crystalline solid we shall eventually reach a point where, though we continue to give heat to the system at the same rate, the temperature ceases to rise. Upon investigation we shall find the solid has begun to melt, and the temperature remains constant until all is melted. This temperature is the melting point.

Freezing Point. If we slowly cool a liquid we shall eventually reach a temperature where, though we continue to abstract heat at the same rate, the temperature ceases to fall. Upon investigation we shall find the liquid has begun to freeze and the temperature remains constant until all is frozen. (This holds only if the solid is crystalline.) This temperature is the freezing point and it is exactly the same as the melting point. The two terms are synonymous and may be used interchangeably. " Point of fusion," " point of solidification " are other synonyms for precisely the same thing.

Amorphous solids have no definite melting points.

Determination of Melting Points. The melting point is a characteristic constant for each crystalline solid and much used for purposes of identification. A convenient way to determine it, using only minute fragments, is as follows: Draw out a thin-walled capillary of 1 mm. or less internal diameter and 6 or 8 cm. long. Put a few small bits of the solid in this and wire it on a thermometer with platinum wires in such a way that the solid is opposite the bulb of the thermometer. Dip the thermometer and capillary in a suitable bath (sulphuric acid is much used owing to its high boiling point) and slowly raise the temperature with a small flame, watching the solid. The beginning of melting is easily detected on the sharp edges of the solid and reading the thermometer at once we have the melting point.

Heat of Liquefaction. The essential difference between the same substance in the solid and in the liquid condition of aggregation is the energy contents. To convert one gram of a solid at its melting point to a liquid at the same temperature we must add a definite

quantity of heat. This quantity of heat is called the heat of liquefaction or of fusion. Of course, to convert one gram of the liquid at its freezing point to a solid at the same temperature exactly the same amount of heat must be abstracted from it.

Molecular Heat of Liquefaction. The amount of heat required to convert a molecular weight in grams of a solid at its melting point to a liquid at the same temperature is called the molecular heat of liquefaction or fusion. It is, of course, the heat of liquefaction times the molecular weight.

	Melting point.	Heat of fusion.
Water	0°	80
Benzene	+ 5.5°	30
Acetic acid	+16.6°	45
Mercury	−38.8°	2.8
Phenol	+40.5°	26
Naphthalene	+80°	36
Lead	+327°	6
Copper	1084°	42

Vapor Pressure at the Melting Point. If we have liquid and solid in contact with each other at the melting point in a closed tube and take care that no heat is given to or taken from the system, we know the quantities of liquid and solid will not alter. The system is in equilibrium. This fact proves that the vapor pressure of the solid must be the same as that of the liquid.

Suppose the vapor pressure of the liquid were greater than that of the solid. It would evaporate until the concentration of the gaseous phase corresponded to that vapor pressure. That concentration would be greater than corresponds to the vapor pressure of the solid, so gas would condense on the solid. This would be followed by more liquid evaporating, and, in time, all the liquid would distill over to the solid. If the solid had a greater vapor pressure than the liquid it would distill in like manner over to the liquid. Thus, if the vapor pressures were not exactly the same, one phase would disappear. It does not disappear, therefore the vapor pressures must be the same.

General Law. This is an illustration of a general law which states that any system which is in equilibrium in one way must be in equilibrium in all ways.

Graphical Representation. These facts can be expressed graphically. In Fig. 38 the curve *ABC* is the vapor pressure curve for

water and *DB* is the vapor pressure curve for ice, both plotted according to the experimental values given on p. 275, but of course on an entirely different scale from that used in Fig. 36.

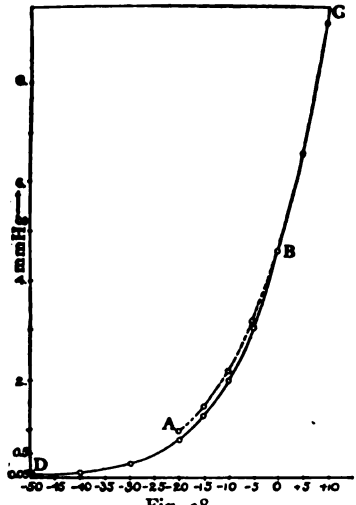


Fig. 38.

The vapor pressure curve for ice, *DB*, cuts the vapor pressure curve for water, *ABC*, at *B*, the melting point. Evidently the melting point must always be given by the intersection of the vapor pressure curves for the solid and liquid phases.

Metastable Conditions. Liquid water may be cooled below its freezing point without freezing provided no trace of the other phase be present. These conditions are represented by the broken line curve, *AB*. It is in a metastable state and a very small thing will cause it to change to a stable condition. It is in a stable condition only in positions along the full line curve *BC*, that is, above the melting point.

It may be seen from the diagram that the substance in a metastable condition has a higher vapor pressure than when in a stable condition at the same temperature. This has been found to be a general law without exception. At a given temperature the stable form of a substance always has the lowest vapor pressure of all forms possible at that temperature.

Experimental Demonstration of Supercooling. The phenomena of supercooling may be conveniently shown with sodium thiosulphate, $Na_2S_2O_3 \cdot 5\,H_2O$ which melts at 48°. Melt enough in each of several test tubes to fill the tubes about half full of the liquid. Close them with loose plugs of absorbent cotton to prevent any crystals of the substance from getting in. They may be kept for months without solidification beginning. Draw out some glass tube as fine as a stout hair, draw it across some solid sodium thiosulphate in such a way as to pick up a crystal or two, which may be too small to see, and insert in one of the test tubes. Crystallization begins at once and simultaneously heat is evolved (the heat of liquefaction), and the contents of the tube grows perceptibly warmer. When the

temperature has risen to the melting point solidification will of course cease, but will proceed until all is solid if heat is conducted away.

Superheated Solid never yet Obtained. Ice is in a stable state anywhere along the full line curve *DB*. This curve is not produced beyond *B* because, for reasons we do not know, it has been found impossible to superheat ice or any other solid above its melting point.

Sublimation. Referring to Fig. 38 we see that ice has measurable vapor pressures at temperatures far below the melting point, and so always evaporates until the corresponding gaseous pressure of water vapor above it is established. This is not exceptional, but general, and all solids evaporate at any temperature, as do liquids, only slower as a rule. When a solid changes directly into a gas, or the converse, without passing through the liquid condition of aggregation we call the process sublimation.

The sublimation of sulphur, of arsenic trioxide, and of iodine are typical and familiar instances. The vapor pressure of camphor is sufficient to produce an easily perceived reduction in the size of a lump in a few hours. Snow vanishes without melting on a cold, windy day.

Ordinarily we think of sublimation only in connection with solids which have particularly high vapor pressures at temperatures below their melting points. But it is clear that we can "sublime" anything by giving it heat, but not enough to raise the temperature to the melting point, and simultaneously removing the vapor, by a suction pump or a current of an indifferent gas, thereby preventing the establishment of equilibrium. For instance, we have only to keep the temperature constant a little below 0° and to keep the pressure of the gaseous water a little below 4.5 mm. to sublime any quantity of ice.

Heat of Sublimation. The number of calories required to change one gram of a solid to a gas at the same temperature is called the heat of sublimation. It is the sum of the heats of liquefaction and of vaporization.

The heat of sublimation multiplied by the molecular weight is the molecular heat of sublimation.

Boiling Point below the Melting Point. In some cases rather curious relationships are brought to light by our vapor pressure diagrams. For instance, in Fig. 39 (not drawn to scale), *ABC* is a vapor pressure curve for a liquid. Where it cuts the horizontal,

MM (which corresponds to 760 mm.) at *C*, we have the boiling point as usually understood. *DB* is the vapor pressure curve of the solid and where it cuts *ABC*, at *B*, we have the melting point.

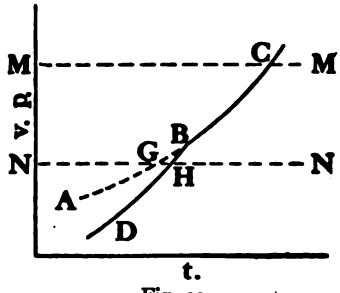


Fig. 39.

Now suppose the nature of the substance is such that its vapor pressure is very high, so high that the horizontal *NN* corresponds to 760 mm. The curve *DB* cuts this horizontal at *H*, that is, the vapor pressure of the solid is 760 mm. before the melting point is reached, and so it will all sublime away without melting. Moreover the curve *AB* cuts this horizontal at *G*. This is by definition the boiling point, the temperature at which the vapor pressure of the liquid equals 760 mm. This boiling point is below the melting point.

We see also from this diagram that we cannot have the liquid in a stable state under a pressure as low as 760 mm. If we put it in an enclosed vessel and raise the pressure, however, let us say to 2000 mm. and that the horizontal *MM* now represents this pressure, and then raise the temperature, the diagram shows us that the substance will behave like most substances, first melting and then boiling. Carbon dioxide is a substance with which these unusual relationships, a "boiling point" below the melting point, are realized.

Volume Change. There is generally a change in volume accompanying a change in state of aggregation. Almost always a substance occupies a greater volume as a liquid than as a solid, but this is not a universal rule, so common a substance as water showing the opposite behavior. Water, freezing to ice, expands, and on this account ice floats.

Effect of Pressure on the Melting Point. The effect of pressure on the melting point is slight, but if melting is accompanied by an increase in volume, an increase in the pressure raises the melting point; if melting is accompanied by a diminution in volume, an increase in the pressure lowers the melting point.

It is very easy to see the logical and necessary connection here. Suppose a substance increases in volume upon melting, as is usually the case. Whatever pressure there may be on the solid resists this volume increase, and an increase in pressure is an additional obstacle

to melting. Applying our kinetic theory, the heat in the solid consists of molecular motion, but the kinetic energy of this is not sufficient to overcome the intermolecular attractions holding the molecules in an orderly arrangement. At the melting point the kinetic energy of the heat motion just barely overcomes these attractions. If, besides this, the heat motion must increase the volume against a high pressure more kinetic energy is needed. The kinetic energy of the heat motion is greater only if the temperature is higher. Therefore under a higher pressure the melting point must be higher. On the other hand, if the substance is a liquid and we cool it we may think of the kinetic energy as opposing the tendency of the intermolecular attractions to hold the molecules in fixed positions in a smaller volume. An increase in pressure also tends to make the volume smaller, *i.e.*, it works hand in hand with the attractions and against the kinetic energy of the molecules. The two forces can overcome more kinetic energy, therefore the substance solidifies at a higher temperature. We reach the same conclusion from either point of view, of course.

If melting is accompanied by a diminution in volume the converse of this reasoning holds and an increase in pressure lowers the melting point. An increase of one atmosphere in pressure upon ice lowers its melting point 0.0074° and, since water is under a pressure of one atmosphere when we determine its freezing point and call it 0°, it follows that water freezes, or ice melts, at +0.0074° in vacuo.*

Triple Point. We may summarize the main facts we have been considering in one diagram, and at the same time show how they are all included in the broad scope of the phase law.

Let us suppose we have a pure solid below its melting point in contact with its own vapor and nothing else, in a cylinder with a piston. The pressure from within on the piston is the vapor pressure of the solid. We have a system with one component and two phases and so have one degree of freedom. We may alter the temperature, but then the pressure automatically takes on a definite value; or we may choose a series of values for the pressure, but we can have them only at the corresponding temperatures. Attempts to alter the pressures by pulling out or pushing in the piston without corresponding alteration of the temperature will not produce the desired result but will cause the total disappearance of one of the two phases. All the conditions under which we can have these two phases in contact

* We shall consider the method of calculating the influence of pressure on melting points in the next chapter.

and in equilibrium are represented by points on the curve *AB* in Fig. 40.

If we raise the temperature we shall reach the point *B* at which the solid melts. Here we have the three phases, solid, liquid, and gas, in contact with each other and in equilibrium. There being but one component and three phases there are no degrees of freedom. We can choose nothing. There is but one set of conditions, a definite pressure, temperature, and concentration, for any pure substance at which we can have it as a gas, liquid, and solid, in contact and in equilibrium. This set of three conditions is what is called the triple point.

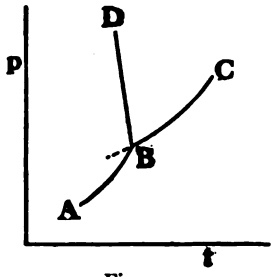


Fig. 40.

If we try to increase the temperature all the solid will melt, *i.e.*, one phase will go out of existence and before we can alter the temperature we shall have only two phases. Then of course we get back one degree of freedom and can choose a series of temperatures, but for each one we have a definite unalterable pressure. All the conditions under which we can have liquid and gas in contact and in equilibrium are represented by points on the curve *BC*.

If, at the triple point, with all three phases present, we try to increase the pressure by pushing in the piston we shall not succeed. We shall merely condense more and more gas until finally the gaseous phase has entirely disappeared. When the piston is in direct contact with the liquid and solid we can indeed increase the pressure. But if we do this holding the temperature constant, if our substance is H_2O we shall melt the ice, for the melting point of H_2O is lowered by increased pressure. If we desire to retain both solid and liquid in contact and in equilibrium under a higher pressure we must also diminish the temperature. We may thus determine a series of pairs of values of temperature and pressure at which we can have solid and liquid in equilibrium and plotting these we obtain the line *BD*. This line then contains all the conditions of equilibrium for the solid and liquid phases. It is drawn with an inclination to the left to show the actual behavior of H_2O.

If our substance belongs to the large majority which increase in volume upon melting and we have the three phases at the triple point and increase the pressure, the gaseous phase will first disappear and then the liquid will freeze. To get back our two phases, liquid

and solid, under the increased pressure we must raise the temperature. In this way we can determine pairs of values and, plotting, obtain a line corresponding to *DB*, but with an inclination to the right.

We thus see we may melt ice at temperatures considerably below its "melting point" by high pressures, and that we may freeze many substances at temperatures above their freezing points by the same means. These effects are not ordinarily met because of the very high pressures required to make much difference in melting points, but they play an important rôle in geological processes wherein pressures are produced by the weights of glaciers and of mountains.

Pressure gauges for high pressures must be filled with a liquid difficult to freeze, otherwise heavy pressure will solidify it at room temperatures.

It will be seen that the curves *BC* and *DB* are the limiting conditions for the liquid phase, and that if we have a pair of values for p and t giving a point falling in the region so bounded, the substance must be a liquid with neither gas nor solid present.

In like manner the curves *AB* and *DB* are the limiting conditions for the solid phase, and if the conditions are represented by a point in this region the substance must be a solid with neither liquid nor gas present.

Lastly, the curves *AB* and *BC* bound the region for a gas and if the conditions give a point in this region the substance must be wholly gas with no trace of solid or liquid present.

Within any one of these regions, manifestly, we can choose a pressure arbitrarily and then, holding this constant, can change the temperature within wide limits. We have then two degrees of freedom. This too is formulated in Gibbs' phase law, for, having one component and but one phase, the law tells us we have two degrees of freedom.

Terminology. A system with no degree of freedom, as our illustration, ice, water, and water vapor, is called invariant or nonvariant, and its conditions for equilibrium are represented by a point. A system with one degree of freedom, of which we have had three illustrations, ice and water vapor, water and water vapor, ice and water, is called univariant or monovariant and its conditions for equilibrium are represented by lines. A system with two degrees of freedom, of which we have had three illustrations, ice, water, and water vapor, is called bivariant, or divariant, and its conditions for equilibrium are represented by areas.

If a system has more than two degrees of freedom we call it multivariant. We shall have illustrations of these systems in our discussion of solubility.

Systems which contain no gaseous phase, such as ice and water and no water vapor, are called condensed systems.

Transformations. One and the same solid may exist in different forms and we have called this polymorphism. We may have carbon as charcoal, graphite, or diamond, phosphorus as red or white phosphorus, sulphur as rhombic or monoclinic crystals (also in other crystalline forms and amorphous), etc. We shall illustrate a number of general principles by use of data obtained for sulphur.

Transition Points. It has been found experimentally that monoclinic sulphur below 95.5° slowly changes to rhombic sulphur and that rhombic sulphur above 95.5° slowly changes to the monoclinic variety. There is then a definite temperature below which one form is stable and the other form is metastable and above which these conditions are reversed. This characteristic temperature is called the transition point. (It is sometimes called the transformation point, sometimes the inversion point.)

Determination of Transition Points. There are several methods by which we may determine transition points. The description of one of these will suffice for our purpose. We make use of what is called a dilatometer, a very simple arrangement like an overgrown thermometer. A reasonable quantity of the solid to be investigated is put in the bulb and then we put in enough of some liquid in which the solid is not soluble to completely fill the bulb and stand at a convenient height in the capillary. The dilatometer is then immersed in a bath and the temperature is gradually raised. The liquid in the capillary rises regularly while the heating is regular. But when the solid substance begins to undergo transformation, there is a volume change, either an increase or diminution in volume, and this becomes apparent by interrupting the regular rate at which the liquid is rising. The temperature of the bath at which this phenomenon is first noted is the transition point. Actually, observations are made with descending as well as ascending temperature and the average of several determinations is taken.

Heat of Transformation. That variety which forms as temperature rises forms with the absorption of heat. This same quantity of heat is given out again when the transformation is reversed. The fundamental and most essential difference between polymorphous

forms is then their energy contents. The number of calories which must be given to one gram of one form to convert it to the next, is called the heat of transformation.

Graphical Representation. The close analogy between transition points and melting points is obvious. It is yet more plain when we draw a vapor pressure diagram and study the phenomena in the light of the phase law. *AB*, in Fig. 41 (not drawn to scale), is the vapor pressure curve for rhombic sulphur. It has not been measured, but in all probability lies about as drawn. *BC* is the vapor pressure curve for monoclinic sulphur. These curves intersect at *B* (95.5°), the transition point. *CD* is the vapor pressure curve for liquid sulphur. It intersects *BC* at *C*, which is then the melting point of the monoclinic variety (120°).

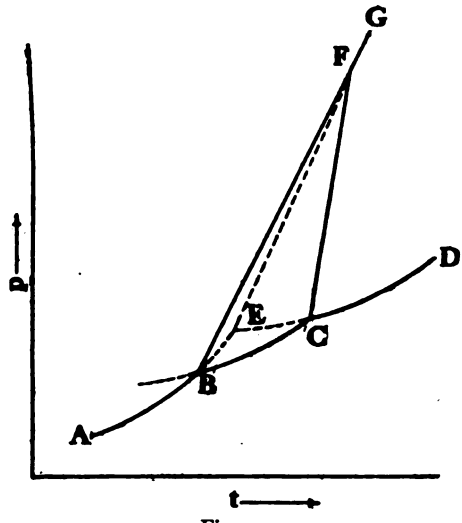


Fig. 41.

Two Melting Points. While we have never yet succeeded in raising a solid above its melting point it is easy to raise it above its transition point, for most transformations in solids occur but slowly. We may then continue curve *AB* to *E*. Between *B* and *E* we have rhombic sulphur in a metastable state. We may supercool liquid sulphur and so prolong the curve *DC* until it cuts *AE* at *E*. This is, clearly, the melting point of rhombic sulphur (114.5°). Sulphur has then two melting points.

On melting, it increases in volume, therefore an increase in pressure raises the melting point. Hence the curve *CF*, which represents the conditions of equilibrium of the univariant system, monoclinic sulphur and liquid, inclines to the right. The transition of rhombic to monoclinic sulphur is also accompanied by an increase in volume and it has been found that the transition point of sulphur is raised 0.05° by an increase of one atmosphere in pressure. The effect is shown by the curve *BF* which contains all the conditions for equilibrium in

the univariant system rhombic-monoclinic sulphur. Actual experiments show that the inclination of *BF* is greater than that of *CF*. Therefore these curves must intersect as at *F*. *F* corresponds to a temperature of 151° and a pressure of 1288 atmospheres. It is a triple point for the invariant condensed system of one component, sulphur, in the three phases, rhombic, monoclinic, and liquid.

Other Triple Points. *B* is a triple point, the three phases being rhombic, monoclinic, and gas. *C* is a triple point, the three phases being monoclinic, liquid, and gas. *E* is a metastable triple point, the three phases being rhombic, liquid, and gas. This melting point is also raised by pressure, and a moment's reflection will make clear that the line representing this effect must pass through *F*.

Prolongation of *CF* beyond *F* would represent metastable equilibrium in the condensed system, monoclinic sulphur and liquid. Metastable, because the curve *FG* representing equilibrium between rhombic and liquid sulphur lies below it. It is a general rule that at any one temperature that variety with the lowest pressure is the stable variety. So at this moderately high temperature and very high pressure the usual conditions are reversed and rhombic instead of monoclinic sulphur is in stable equilibrium with the liquid. These considerations are of particular value to mineralogists, furnishing plausible explanations for the occurrence in nature of varieties and of crystal forms which we cannot readily reproduce in the laboratory.

The figure is most informing and should be studied carefully. For instance, we can see at once that the conditions for the stable existence of monoclinic sulphur are circumscribed on all sides. The only conditions under which we can have it (stable) are represented by positions within the area of the triangle *BCF*. We can have rhombic sulphur at any pressure and temperature represented by positions in the area bounded by *ABFG*, liquid sulphur within the area bounded by *DCFG*, gaseous sulphur within the area bounded by *ABCD*.

A full understanding of everything about this diagram will make it easy to understand much more complicated diagrams which have been constructed for other systems with more components.

The Transformation of Tin. Tin exists in two forms. White tin is the form with which we are most familiar and gray tin is a noncoherent powder. The transition temperature is at 20° and the white variety is stable only above this temperature. It may, however, be much supercooled as is proved by the innumerable tin roofs

which endure the low temperatures of winter without changing to the gray variety. Such a roof is, however, in a metastable state and minute particles of gray tin, the other phase, will start the change. Or, in extremely cold weather, the limits of supercooling may be overpassed and the change may begin spontaneously. Then the tin plate becomes covered with peculiar gray spots. The area about these spots consists of this pulverulent tin, without coherence, and wholly useless as a protective coating. This process ruins a roof or any other tin plate and is aptly called the " tin pest."

White tin below 20° in contact with a solution of " pink salt" (tin ammonium chloride) transforms rapidly.

Velocity of Transformation. The velocity of transformation from one solid variety to another varies much. For instance, tetrabrommethane changes as rapidly as a solid melts, while, on the other hand, graphite and diamond change so slowly that we do not know where the temperature of change is, nor which of these is the stable variety at ordinary temperatures.

Unknown Transition Points. We know substances which exist in two varieties, each variety having its own melting point, and yet showing no transition point. The plausible explanation for these facts is contained in Fig. 42. *ED* is the vapor pressure curve for liquid benzophenone, and on its prolongation through *B* to *F* it is in a metastable state. *CD* is the vapor pressure curve for one solid variety and *D* is its melting point (48°). There is a second solid variety, with higher vapor pressures (therefore metastable), and its vapor pressure curve is represented by the broken curve *AB*. Where this cuts the liquid curve, at *B*, we have the melting point of this variety (26°). Both solids melt before their vapor pressure curves intersect. Such intersection is the transition point, and this explains the fact that we have not as yet determined it. It will be observed that if the two curves were continued they would intersect somewhere about *G*, which would then be the transition point. They are not prolonged because we cannot heat a solid above its melting point.

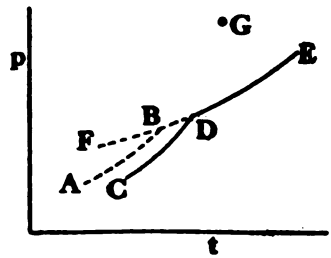


Fig. 42.

Least Stable Variety Forms First. It might seem that when such a liquid solidifies the stable variety should always form and that,

therefore, polymorphous forms should be impossible. But we have found it to be a general rule that when a change occurs, and several varieties with different vapor pressures are possible, that one with the highest vapor pressure is the most apt to form. The vapor pressure drop tends to be as small as possible; the least stable variety forms first. This may continue indefinitely if no trace of the other phase is present. On the other hand, metastable conditions sometimes break down spontaneously and then we have the stable form.

Solidification May Follow Melting. This figure also explains a curious phenomenon sometimes observed. A few substances are known which, as the temperature is slowly and regularly raised, first melt, then solidify, then melt a second time. A metastable solid melts as at *B*. The liquid is metastable and the second solid variety may form before its melting point is reached. Further heating then brings us to the melting point of this variety, as at *D*.

Monotropy and Enantiotropy. Substances like benzophenone, with two solid varieties and two melting points, but whose transition points are unknown, are called monotropic. Substances like sulphur with two melting points and a known transition point are called enantiotropic. One substance may exist in three or more varieties and display the phenomenon of enantiotropy with respect to a pair or pairs of forms and monotropy with respect to other pairs.

Thermodynamic Potential. When substances change from one phase to another, either from one condition of aggregation to another or from one form to another, the change is due to energy, and whether the process will occur or not, and in which direction, is determined by the intensity factor. There is no essential difference between these processes and chemical reactions; therefore the measure of the tendency to change is a measure of chemical potential. It is also in these cases often called the thermodynamic potential.

We have devoted as much time and space as we can afford to the consideration of heterogeneous equilibrium in systems of one component and have brought out the fundamental principles involved. This is the main purpose of this book and no one topic is exhausted before we must pass on to the next.*

* For additional information the reader is referred to "The Phase Rule," by W. D. Bancroft, 248 pp. (1897). "The Phase Rule," by Alexander Findlay, 313 pp. (1904). "Die Heterogenen Gleichgewichte," by H. W. Bakhuis Roozeboom, first part, 217 pp. (1901); second part, 467 pp. (1904); third part (continued by F. A. H. Schreinemakers), 312 pp. (1911).

CHAPTER XXII

SOME ELEMENTARY THERMODYNAMIC DEDUCTIONS

THAT branch of science which deals with conversions of heat energy into mechanical energy and the converse is called thermodynamics. The facts lend themselves peculiarly well to succinct yet adequate and accurate expression in mathematical formulæ. Many of these formulæ are of such a general nature they apply to all processes. We have reached a point in our study where it is desirable that we should have a knowledge of the simplest of these, and of the methods by which they were derived, both to round off some of the topics already considered and also as starting points for future considerations.

The basis of all thermodynamical deductions is the two laws which were stated so fully in Chapter III that no repetition is necessary. The subject, as ordinarily presented, consists of a number of these mathematical deductions and of little, if anything, else; that is, it is almost purely deductive.

Formulation of the First Law. Suppose we convert A gram-centimeters of work into heat and obtain W calories. J is a proportionality factor, the mechanical equivalent of heat. Then $A = JW$, a mathematical expression of the law of the conservation of energy. This particular application of the universal law is called the first law of thermodynamics.

Suppose we have a system consisting of any set of substances, capable of entering into a process. Let U_1 equal the total internal energy of the system before the process begins and let U_2 equal its total internal energy after the completion of the process. Then $U_1 - U_2$ equals the difference in internal energy due to the process. Let A equal the quantity of work which was done and Q the quantity of heat, measured in the same system of units as A, say ergs, which was given out by the system during the process. Both work and heat must have come from the internal energy, therefore $U_1 - U_2 = A + Q$. It is customary to denote change in internal energy by U; then

$$U = U_1 - U_2, \text{ and } U = A + Q \qquad (1)$$

another mathematical expression of the first law of thermodynamics.

Of course part of the process may consist in doing work on the system, as in compressing a gas, and the internal energy may increase instead of diminishing during the process. Again, the process may absorb heat as well as do work. In such a case the sign of Q would be changed. A moment's reflection as to whether work is done *on* the system or *by* the system, whether heat is given *off* by the system or given *to* it, will determine the signs before the quantities in the above equation, and will fit it to any process.

Suppose the initial and final conditions of a given system to be the same in two cases, but that in the first case we reached the end by one route and in the second by another. According to the law, the energy difference must be the same in each case, for if it were not, we could let the system do work by the harder route and then force it back to its initial conditions by the easier route and thus gain more than an equivalent of the work we put in at each complete revolution, or cycle as we call it. We should thus be creating energy, and the first law states that this is impossible. Then we may say, provided the initial and final conditions are the same, the process or processes, one or many, by which we pass, make no difference in the total energy change. Another way of expressing the same thing is to say the algebraic sum of the energy changes, few or many, between given conditions, is a constant. This finds many important applications. In thermochemistry it appears as the law of constant heat summation (see Chapter XXVII.)

Work Done by a Gas Expanding Isothermally. Let us consider a very simple process. Suppose a gas of volume v_1, in a cylinder with a frictionless piston, expands isothermally (temperature constant), while the pressure also remains constant, until it occupies the volume v_2. It pushes, with a pressure, p, through a distance corresponding to the increase in volume and so it does work, A, equal to $p(v_2 - v_1)$.

As a matter of fact, when a definite quantity of a gas expands isothermally the pressure does not remain constant but diminishes as the volume increases; yet, if we consider an exceedingly small increase in volume, dv, the pressure may be considered as practically constant. The exceedingly small quantity of work done during this change may be denoted by dA. Then $dA = pdv$.

If we are dealing with an ideal gas, $pv = RT$ or $p = \frac{RT}{v}$. Substituting this value in the above equation, we have $dA = \frac{RT}{v}dv$. Inte-

grating this expression we obtain $A = RT ln\, v + C$.* The integration constant may be eliminated as follows: If v, the final volume, equals v_1, the original volume, there is no change in volume and no work is done; $A = 0$. Then $0 = RT ln\, v_1 + C$ and $C = -RT ln\, v_1$. Substituting this value for C we obtain,

$$A = RT ln\, v - RT ln\, v_1 = RT\,(ln\, v - ln\, v_1) = RT ln \frac{v}{v_1}. \qquad (2)$$

The expansion we are considering being from v_1 to v_2 the formula becomes $A = RT ln \frac{v_2}{v_1}$ and from this we readily derive the formula by which to calculate the work corresponding to a change from an original pressure p_1 to a final pressure p_2. From the gas law we have $v_1 = \frac{RT}{p_1}$ and $v_2 = \frac{RT}{p_2}$. Substituting these values in our equation we have

$$A = RT ln \frac{RT}{p_2} \times \frac{p_1}{RT} \quad \text{or} \quad A = RT ln \frac{p_1}{p_2}. \qquad (3)$$

A graphical representation is helpful in following the reasoning by which this formula is derived. In Fig. 43 volumes are laid off on the horizontal and pressures on the vertical. p_1v_1 are the initial and p_2v_2 are the final conditions. Assuming the gas to be ideal and the temperature constant, $p_1v_1 = p_2v_2$ and the curve is a right-angle hyperbola. When the volume increases a small amount, dv, the gas does work equal to dv times the pressure. This work is represented by the area enclosed by v_1Aab. This area is almost exactly $p\ dv$, and the smaller we make dv the more accurate is the expression. All the work done by the gas in expanding isothermally from p_1v_1 to p_2v_2 is represented by the area enclosed by v_1ABv_2. We may imagine this as made up

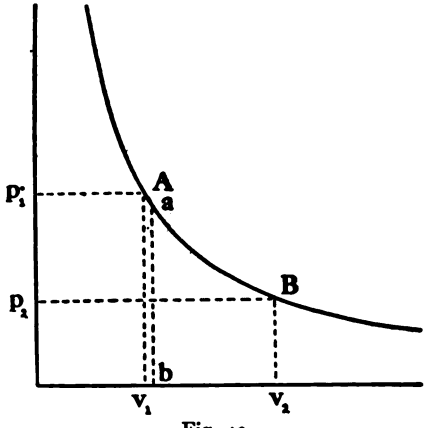


Fig. 43

* $ln\, x \times 0.434\,29 = \log x$ or $\log x \times 2.3026 = ln\, x$ (see Appendix).

of a great many small slices the area of each being $p\,dv$. Therefore the whole area, or the whole work,

$$A = \int_{v_1}^{v_2} p\,dv.$$

Since $pv = RT$, $p = \frac{RT}{v}$, and substituting, $A = RT\int_{v_1}^{v_2}\frac{dv}{v} = RTln\frac{v_2}{v_1}$, the formula sought.

Amount of Heat Which Can Be Converted to Work. Suppose we have a quantity of an ideal gas in a cylinder with a frictionless piston, and that we have two large reservoirs of water, one at temperature T and the other at the slightly higher temperature $T + dT$. Put the cylinder in the first and the volume of the gas becomes v_1. Compress the gas to volume v_2 so slowly the heat is taken up by the reservoir and the temperature of the gas does not change. The work required for this compression is $A = RTln\frac{v_1}{v_2}$. Call the amount of heat equivalent to this work, Q. As our gas is supposed to be ideal, $p_1v_1 = p_2v_2$ and there is no change in its internal energy, so

$$Q = RTln\frac{v_1}{v_2}. \tag{4}$$

Now transfer to the second reservoir and, holding the volume constant, wait until the temperature of the gas has become $T + dT$. If K be the heat capacity of the gas it will take up $K\,dT$ calories from the reservoir. Now let the gas do work so slowly it takes up heat from the reservoir at the same rate and remains at the constant temperature $T + dT$, until its volume becomes v_1 again. It has done work equal to $A + dA = R(T + dT)\,ln\frac{v_1}{v_2}$, and since its internal energy remains the same it has taken the equivalent of this work in the form of heat from the reservoir or,

$$Q + dQ = R(T + dT)\,ln\frac{v_1}{v_2}. \tag{5}$$

Now put the machine back in the first reservoir and wait until it has resumed its original temperature, T. In so doing it gives the reservoir an amount of heat $K\,dT$ and is back in exactly its original condition.

By this reversible cyclical process we have transferred a quantity of heat $Q + K\,dT$ from the temperature $T + dT$ to the lower temperature T. We did work on the gas equivalent to Q and the gas did

work equivalent to $Q + dQ$ and so dQ is the amount of heat equivalent to the gain in work, dA, when $Q + K\,dT$ of heat is transported from the temperature $T + dT$ to the temperature T. $K\,dT$ is so small in comparison with Q it may be disregarded; therefore,

$$Q = Q + K\,dT.$$

Expand equation (5) and we have,

$$Q + dQ = RT ln \frac{v_1}{v_2} + R\,dT\,ln \frac{v_1}{v_2}.$$

Subtract equation (4) and we have,

$$dQ = R\,dT\,ln \frac{v_1}{v_2}.$$

Divide this by equation (4) and we get,

$$\frac{dQ}{Q} = \frac{R\,dT\,ln \frac{v_1}{v_2}}{RT ln \frac{v_1}{v_2}} = \frac{dT}{T},$$

or
$$dQ = Q\frac{dT}{T} \quad \text{or} \quad dA = Q\frac{dT}{T}. \tag{6}$$

This is the fundamental mathematical expression of the second law of thermodynamics.

In words, this formula tells us that the fraction of all the heat transported which can be converted into useful work by a perfect machine is the same as the fraction given by placing the difference in temperature in the numerator and the lower temperature on the absolute scale in the denominator.

Economic Coefficient. Let $Q' = Q + dQ$; then $dQ = Q' - Q$. Let $T' = T + dT$; then $dT = T' - T$. Substitute in (6) and get,

$$\frac{Q' - Q}{Q} = \frac{T' - T}{T}.$$

Multiplying out we have $Q'T - QT = QT' - QT$, or $Q'T = QT'$, or $\frac{Q}{Q'} = \frac{T}{T'}$, or $1 - \frac{Q}{Q'} = 1 - \frac{T}{T'}$, or $\frac{Q' - Q}{Q'} = \frac{T' - T}{T'}$. (Remember that T' is the higher, T the lower temperature, and that Q' is the whole of the heat and Q is the heat not converted into work.) This value, $\frac{Q' - Q}{Q'}$, is often called the economic coefficient, expressing, as it does, the maximum fraction of the whole of the heat transferred which can

be converted to work by the most ideally perfect machine working between the given temperatures.

An illustration will show its utility. Suppose a perfect steam engine to be furnished with steam at 200° while the condenser is at 100°. $T' = 473$, $T = 373$. $\frac{T' - T}{T'} = \frac{100}{473}$ or a little more than one-fifth of the total heat transferred may be converted to work by the most perfect, frictionless engine. Of course all machines are much less efficient than this.

Suppose the explosions in a gas engine raise the temperature of the products of combustion to 1000°, and suppose the temperature of the exhaust to be 100°. Then we have $\frac{1273 - 373}{1273} = \frac{900}{1273}$ or almost three-fourths of all the heat transferred might be converted to useful work by an ideally perfect engine. Of course realization is far short of this, but here we have the underlying reason for the relatively high efficiency of internal combustion engines.

Calculation of Heat of Vaporization. Suppose we have a molecular weight in grams of a liquid at some temperature T. The pressure is the vapor pressure at that temperature, p, and the volume is v. We shall imagine it in a cylinder with a frictionless piston just resting on the surface of the liquid with a pressure equal to the vapor pressure p. Put the cylinder in a large tank of water at the temperature $T + dT$. This causes the pressure to rise to $p + dp$ and of course that pushes back the piston. Heat is obtained from the tank, and the process will not stop until all the liquid has become vapor. Let λ equal the amount of heat so taken up; it is by definition the molecular heat of vaporization. Let v' equal the much larger volume now occupied by the substance as a gas. Now transfer the cylinder to a tank of water at temperature T and allow the gas to liquefy. In the process it will give up the same quantity of heat, λ, to the tank at this temperature. We have thus transferred the total quantity of heat, λ, from $T + dT$ to T. In expanding the system did work equal to $(v' - v)(p + dp)$, in condensing, work was done on it equal to $(v' - v)\,p$. Then $(v' - v)(p + dp) - (v' - v)\,p$ = gain in work $= dA$. Multiply out and cancel and we obtain $(v' - v)\,dp = dA$. But from equation (6) we know $dA = Q\frac{dT}{T}$. Therefore, $(v' - v)\,dp = \lambda\frac{dT}{T}$. This is called the Clausius-Clapeyron formula.

The volume of a molecular weight in grams of a liquid is negligible

as compared to its volume as a gas. (For instance 18 cm^3 H_2O liquid would occupy $22\,400 \times \frac{373}{273}$ at 100° and 760 mm.) So we may write,

$$v' \, dp = \lambda \frac{dT}{T} \quad \text{or} \quad \lambda = v' T \frac{dp}{dT}. \tag{7}$$

In words, the molecular heat of vaporization is equal to the volume occupied by the substance as a gas times the absolute temperature at which the vaporization is carried out times the coefficient of increase in vapor pressure with increase of temperature. Thus we may calculate the heat of vaporization from the inclination of the vapor-pressure curve. But now this v' is the volume of the substance as a gas, and if the conditions are such that the gas laws apply we have $pv = RT$ or $v' = \frac{RT}{p}$. Substituting in (7) we have,

$$\lambda = \frac{RT^2}{p} \frac{dp}{dT}. \tag{8}$$

This is the same as

$$\lambda = RT^2 \frac{d \ln p}{dT}. \tag{9}$$

To illustrate the way in which this formula may be applied let us calculate the molecular heat of vaporization of water at 100°. The vapor pressure of water at 99.5° is 746.52, at 100.5° it is 773.69 mm. Hence $\frac{dp}{dT} = 773.69 - 746.52 = 27.17$ mm.* $= 0.035\,75$ atmospheres. $R = 1.98$ cal. (see Chapter XXVII). $p = 1$ and $T = 373$. Therefore,

$$\lambda = 1.98 \times 373^2 \times 0.035\,75 = 9849 \text{ cal.}$$

The heat of vaporization of one gram of water at 100° is found experimentally to be 538.7 cal. Multiply this by 18 to obtain the molecular heat of vaporization and we have 9700 cal. The result of the calculation is in only fair agreement with the experimental result, but we omitted several corrections. We assumed the gaseous water occupied the full theoretical volume, whereas experimentally it has been found to occupy a smaller volume (gases are too compressible near their points of condensation). If we had utilized the actual volume the results would have checked better.

* See W. Nernst and A. Schönfliess, "Einführung in die Mathematische Behandlung der Naturwissenschaften," fifth edition (1907), p. 287. This book (371 pp.) is recommended to those desiring to study the mathematical treatment of our subject.

Calculation of Change of Melting Point upon Change of Pressure. The formula which we developed for the heat of vaporization applies by exactly the same process of reasoning to the heat of fusion or liquefaction. Let ρ equal the molecular heat of fusion and v the increase in volume upon melting. Then equation (7) becomes, upon inserting these quantities,

$$\rho = vT\frac{dp}{dT} \tag{10}$$

or

$$dT = \frac{vT}{\rho}dp.$$

When ice changes to water there is a diminution of volume, and so v is a minus quantity. Temperature and heat of fusion are both plus quantities. Therefore, if dp is a plus quantity, dT must be a minus quantity. In other words an increase of pressure must lower the melting point of ice. This is the fact found by experiment.

We may readily calculate how much an increase in pressure amounting to one atmosphere will lower the melting point of ice. In this case, $T = 273$, $\rho = 80$ cal. 80 cal. $= 80 \times 42\,660$ gram-centimeters. One gram of water becoming ice increases its volume 0.09 cm^3. $dp = 76 \times 13.59 = 1033.3$ grams per cm^2. Substituting in (10) we have, $dT = \frac{0.09 \times 273}{80 \times 42\,660} \times 1033.3$, and $dT = 0.007\,43°$; *i.e.*, an increase of one atmosphere in pressure lowers the melting point of ice by 0.007 43°. This is the value found experimentally.

Temperature Coefficient. Suppose a process takes place in a system at the constant temperature T, and that this involves a loss, U_T, in the internal energy. After this, the system is warmed to the temperature $T + dT$ while the volume is held constant so that no external work is done. If K_2 represents the heat capacity of the products of the process, $K_2 dT$ calories of heat are added to the system. The system finally contains $U_T - K_2 dT$ less energy than at the beginning.

Now start again with the original system and warm it to $T + dT$ before permitting the process to occur. If K_1 represents the heat capacity of the initial substances we must give the system $K_1 dT$ calories. Now permit the process to proceed to the same final conditions as before. The loss in internal energy due to the process is U_{T+dT}. The total loss by this second route is $U_{T+dT} - K_1 dT$ and as initial and final conditions are the same in both cases,

$$U_T - K_2 dT = U_{T+dT} - K_1 dT, \text{ or } K_1 - K_2 = \frac{U_{T+dT} - U_T}{dT}.$$

As dT is an exceedingly small quantity, it is reasonable to suppose that the difference between the internal energy changes, $U_{T+dT} - U_T$ is also a very small quantity, appropriately represented by dU. Then

$$K_1 - K_2 = \frac{dU}{dT}. \qquad (11)$$

dU is the small change in energy manifestation due to the small change dT in the temperature, and so $\frac{dU}{dT}$ is the temperature coefficient of the process. Thus we have deduced that the temperature coefficient of any process is measured by the difference in heat capacities of the initial and final substances.

Interesting conclusions may be drawn from this equation (11) when applied to a chemical reaction. Suppose the process just outlined consists in a reaction of $A + B$ to form $C + D$. Then K_1 is the heat capacity of the system $A + B$, and K_2 is the heat capacity of the system $C + D$. All changes in internal energy may be measured in terms of heat and we may write dQ for dU. Then equation (11) is the same as $K_1 - K_2 = \frac{dQ}{dT}$ dQ is the difference in the heat of the reaction when it occurs at the temperature $T + dT$ instead of at T. and $\frac{dQ}{dT}$ is the temperature coefficient of the heat of reaction.

It follows from the equation that if the specific heats of the reacting substances are the same as the specific heats of the products, $K_1 = K_2$ and the temperature coefficient becomes equal to o. No matter what the temperature, the reaction proceeds with the evolution of the same amount of heat. It has then the same tendency to react, the same chemical potential, at all temperatures.

If the heat capacity of the products is less than that of the reacting substances, the coefficient is positive and the tendency to react, the chemical potential, is greater the higher the temperature. Also, the higher the temperature the more exothermic is the reaction.

If the heat capacity of the products is greater than that of the reacting substances, the coefficient is negative and the tendency to react, the chemical potential, is less the higher the temperature. At a sufficiently high temperature such a reaction would cease to be exothermic.

More of the deductions of thermodynamics might profitably be included, but these are the most essential and must suffice.*

Such deductions are as certain as the fundamental principles or facts from which they start, provided no mistakes are made in the mathematical steps, and provided no unjust fiable hypotheses are introduced in the course of the reasoning. They are so satisfactory to the critical mind it is hardly to be wondered at that they are increasing in favor. One might hesitate to say they are becoming popular. But there is evidence that we are in danger of overestimating them. They are as certain as the premises, but not more so, and those premises are the result, first of actual experiment, and second of induction. The deduction follows as the third step in right thought, and experimental verification should follow as the fourth. One must not forget that study of objective sciences should begin with experiment and end with experiment. Thus these highly cherished thermodynamic reasonings form but a quadrant of the wheel of scientific progress.

* For additional information the reader is referred to "Treatise on Thermodynamics," by Max Planck, translated by Alexander Ogg, 272 pp. (1903).

CHAPTER XXIII

VAPOR PRESSURE OF SOLUTIONS

DISSOLVE a substance in any solvent and the vapor pressure of the solvent is invariably lessened. The vapor pressure of the solution is, however, the sum of the vapor pressures of the solvent and solute. Therefore it may be greater, less, or equal to that of the pure solvent. To understand this more clearly think of a solution containing *A* and *B*. The vapor pressure of *A* is less because of the presence of *B* and that of *B* less because of the presence of *A*. But the sum of these lessened vapor pressures may be greater, less, or equal to either one.

The Case of two Liquids. When two liquids are mutually insoluble, the vapor pressure of a mixture of them is the sum of their individual vapor pressures and greater than either alone.

If two liquids are mutually soluble in all proportions we have three typical cases:

1. Starting with the vapor pressure of pure *A*, as more and more *B* is added, the vapor pressure of the mixture rises to a maximum and then falls to the vapor pressure of *B*. This is shown graphically by curve *AB* in Fig. 44. The left-hand vertical corresponds to 100 per cent *A* and 0 per cent *B*, the right-hand vertical to 0 per cent *A* and 100 per cent *B*. Thus every possible composition from pure *A* to pure *B* is represented by positions on the horizontal. The middle

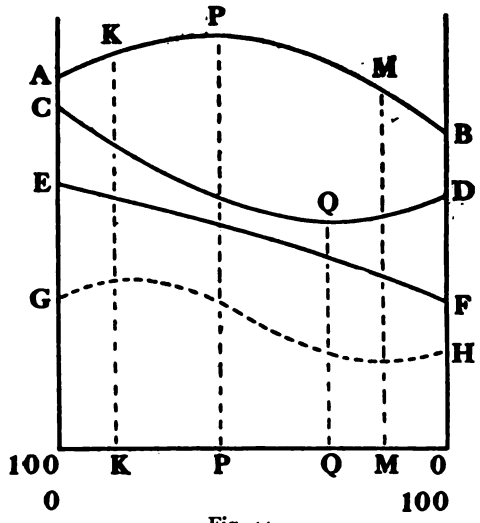


Fig. 44.

point, for instance, corresponds to 50 per cent A and 50 per cent B. The vapor pressures of the different solutions are laid off as vertical heights, and curve AB shows a maximum vapor pressure for about 60 per cent A and 40 per cent B.

2. Starting with the vapor pressure of pure C, upon adding D we observe diminishing vapor pressures to a minimum, and then an ascension to the vapor pressure of pure D, as shown in curve CD.

3. Starting with the vapor pressure of pure E, as we add F we find a gradual decrease in vapor pressure to that of F with neither maximum nor minimum, as shown in curve EF.

4. We might have a pair of substances showing both a maximum and a minimum, as shown in curve GH, though no such case has ever yet been found.

The Theory of Fractional Distillation. The vapor rising from a mixture is, in general, of a different percentage composition from that of the liquid, and since whatever has the greatest vapor pressure will vaporize first, the composition of the vapor will differ from that of the liquid in the sense of the rising portions of the curves in Fig. 44. For instance, if we have a solution containing 90 per cent A and 10 per cent B its vapor pressure will be the vertical height KK. At the point K the ascending part of the curve corresponds to more B and less A, therefore the gas above this solution will contain more B and less A than the liquid. If we have a solution containing 10 per cent A and 90 per cent B its vapor pressure will be the vertical height MM. At the point M, the ascending part of the curve corresponds to more A and less B, and so the vapor will contain more than 10 per cent A and less than 90 per cent B. The same reasoning applies to all the curves and it is not necessary to be more explicit.

Distillation. These considerations and this figure tell us just what will happen if we attempt to distill these mixtures. Suppose we have the 90 per cent A, 10 per cent B mixture; clearly, the tendency will be to get as distillate a solution of composition corresponding to the maximum vapor pressure PP and purer and purer A will remain behind. If, at the beginning, we have the 10 per cent A, 90 per cent B mixture we shall again tend to have the maximum vapor-pressure mixture PP as a distillate, but this time pure B as a residue.

If the liquids are like CD, starting with 90 per cent C and 10 per cent D, we shall tend to have pure C as a distillate and the mixture with minimum vapor pressure QQ as a residue. If we start with 10 per cent C and 90 per cent D we shall tend to have pure D in the

distillate and the same solution with minimum vapor pressure *QQ* as a residue. So only in case the substances behave as represented by *EF*, showing neither a maximum nor a minimum vapor pressure, can we hope to effect a complete separation by fractional distillation.

Mixtures with Constant Boiling Points. If we have a solution of *A* and *B* in just the right proportions for the maximum vapor pressure, this mixture will distill over at a constant boiling point as if it were a pure substance. A mixture of about 70 per cent propyl alcohol and 30 per cent water behaves in this way. This maximum vapor pressure corresponds to a minimum boiling point.

If we have a mixture of *C* and *D* in the right proportions for the minimum vapor pressure it has a constant (maximum) boiling point and distills over unaltered like a pure substance also. Sixty-eight per cent nitric acid and 32 per cent water is an illustration of this type.

Constant Boiling-point Mixtures not Chemical Compounds. It was thought that the constancy of the boiling points proved these mixtures to be chemical compounds, hydrates. But the argument is not satisfactory, for these mixtures do not contain their constituents in the stoicheiometric proportions and so long as we retain our present definition of chemical compound this excludes these mixtures. Moreover, and more conclusive, if we alter the pressure, thus altering the temperature at which ebullition begins, the proportions of the constant boiling mixture are altered also. This could not happen if these mixtures were really chemical individuals.

When Vapor Pressure of the Solute is Negligible. When a solid is dissolved in a liquid the vapor pressure of the solid is usually negligible and the vapor consists of practically pure solvent as a gas. In these cases exceedingly interesting regularities have been discovered.

Fig. 45.

Experiment. Invert four barometer tubes over mercury. By means of pipettes with curved ends, put a little pure ether in the first, a little of a solution of 12.2 g. of benzoic acid in 100 g. ether in the second, a little of a solution of 24.4 g. benzoic acid in 100 g. ether in the third. After a short time the levels of the mercury will stand as shown in Fig. 45. The difference in level

between 4 and 1 is the vapor pressure of pure ether. The difference in level between 2 and 1 is the lowering of the vapor pressure due to the presence of 12.2 g. of the solute. The difference in level between 1 and 3 is the lowering of the vapor pressure due to the presence of 24.4 g. of the solute in the same volume. It is found that this lowering is twice the first. This is one illustration of a general fact, that the lowering of the vapor pressure is directly proportional to the concentration of the solute.*

Lowering at Different Temperatures. For the same solution the lowering of the vapor pressure at any temperature is always the same fraction of the vapor pressure of the pure solvent at that temperature. In Fig. 46, *DA* is the vapor-pressure curve for a pure solvent and *EB* the vapor-pressure curve for a solution in that solvent. The length of the vertical *FD* is the vapor pressure of the pure solvent and the length of *FE* is the vapor pressure of the solution, the length *ED* is the lowering of the vapor pressure due to the presence of the solute, all at temperature *F*. At temperature *C*, we have the vapor pressure of pure solvent = *CA*, of solution = *CB*, and lowering of the vapor pressure = *BA*. Now the statement at the beginning of this paragraph may be expressed in terms of these dimensions and we have, $\frac{BA}{CA} = \frac{ED}{FD}$.

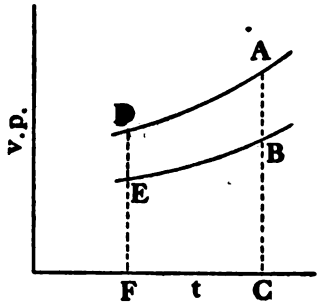


Fig. 46.

General Formulation. The above are limiting laws, holding the better the more dilute the solutions. They are ordinarily formulated as follows:

Let p = the vapor pressure of the solvent.
p' = vapor pressure of the solution.
g = the amount of solute in grams.
r = a constant, dependent on the nature of the solvent and denoting the lowering produced by one gram of the solute in a definite quantity of the solvent.

Then $\frac{p - p'}{p} = rg$.

* This experiment is taken from "The Elements of Electrochemistry," by R. Lüpke, translated by M. M. P. Muir, p. 95.

Historical. The exceptional behavior of water solutions, which we now plausibly explain with the assistance of the dissociation theory, retarded the development of these generalizations. But Raoult found as a result of his experiments with substances other than water the following two fundamental laws:

Equimolecular quantities of different solutes in a definite quantity of one solvent produce the same lowering of the vapor pressure.

A definite quantity of a solute in equimolecular quantities of different solvents produces the same lowering of the vapor pressure.

These laws are limiting laws, holding the better the more dilute the solutions.

Formulation. We formulate them as follows:

Let G = weight in grams of solvent.
g = weight in grams of solute.
M = molecular weight of solvent.
m = molecular weight of solute.

Then $\frac{G}{M}$ = amount of solvent in terms of molecular weights; denote this fraction by N.

$\frac{g}{m}$ = amount of solute in terms of molecular weights; denote this fraction by n.

Then these laws may be expressed as follows:

$$\frac{p - p'}{p} = \frac{n}{N}.$$

Or, in words, the lowering of the vapor pressure, expressed as a fraction of the vapor pressure of the pure solvent, is directly proportional to the number of molecules of the dissolved substance and inversely proportional to the number of molecules of the solvent.

In this form the expression obviously cannot hold because, according to this formula, if one molecule of solute be dissolved in one molecule of solvent $\frac{n}{N} = 1$, that is, the lowering is the total vapor pressure which would leave a vapor pressure of o and this is never realized.

Improved Formula. The experimental facts are much better expressed if we consider everything present, both solvent and solute, to be acting as solvent, which makes the denominator $N + n$, and so we reach the preferable formula

$$\frac{p - p'}{p} = \frac{n}{N + n}.$$

Let us now substitute $\frac{G}{M}$ for N and $\frac{g}{m}$ for n. Simplifying, we obtain,

$$\frac{p - p'}{p} = \frac{gM}{Gm + gM}.$$

We can determine p, p', g, and G experimentally and then can calculate either M or m if we know the other. This is the basis of our methods for determining the molecular weights of dissolved substances from the lowering of the vapor pressure they produce.

Since the laws hold best for dilute solutions we should confine ourselves to these. This means the lowering of the vapor pressure is a small quantity and practically it is found to be rather difficult to determine it with sufficient accuracy. We have, however, an exceedingly ingenious method of getting around this difficulty.

The raising of the boiling point due to the presence of a solute is, for dilute solutions, directly proportional to the lowering of the vapor pressure. This can be seen at a glance from Fig. 47. A is a vapor-pressure curve for a pure solvent, B for this solvent containing a solute at concentration x, C for this solvent containing the same solute at concentration y. The broken line horizontal corresponds to the prevailing atmospheric pressure. Then, by definition, a is the boiling point of the pure solvent, b of the first, and c of the second solution. For dilute solutions the curves A, B, and C are practically parallel and therefore we have the proportion, $ad : ab = ae : ac$. But ad and ae are the lowerings of the vapor pressure, and ab and ac are the raisings of the boiling point, so the direct proportionality between these quantities is demonstrated. In case of concentrated solutions these curves are not parallel and corresponding deviations from this simplest case occur.

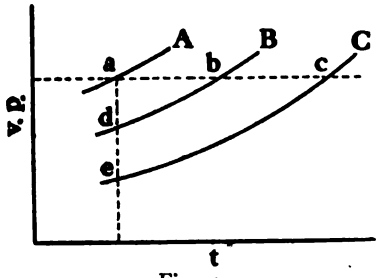


Fig. 47.

The Molecular Raising of the Boiling Point. In actual determinations of molecular weights by the boiling-point method we use a formula somewhat different from that just given but based on the same laws.

The increase in the boiling point produced when a molecular weight in grams of any solute is dissolved in a definite quantity of

one solvent is a constant. For convenience we adopt as unit quantity 100 grams of solvent, and we either calculate or determine experimentally the number of degrees the boiling point would be raised if, in this 100 grams of solvent, we dissolved one molecular weight in grams of a solute. This constant we call the molecular raising of the boiling point and denote it by K. It is different for different solvents and is, after all, a theoretical value because, in the first place, we seldom can make so concentrated a solution and, in the second place, if we did, the solution would be too concentrated for the laws to apply.

In determining this value experimentally we dissolve but a small fraction of a molecular weight (say $\frac{1}{100}$ or $\frac{1}{1000}$ of a molecular weight) in the unit quantity (100 grams) of the solvent. We determine the elevation of the boiling point produced by this amount and then multiply this observed elevation by 100 or by 1000, by the denominator of the fraction, in other words. The result so obtained is our constant K, the molecular raising of the boiling point for that solvent.

Formula. Suppose n equals the actual number of molecular weights or the fraction of a molecular weight of solute which we dissolve, and suppose that the observed elevation of the boiling point in degrees, or fraction of a degree, is Δ. Then $\Delta = Kn$. $n = \frac{g}{m}$. Therefore $\Delta = K\frac{g}{m}$. But we do not always use just 100 grams of our solvent. If we used 1 gram, we should have 100 times the effect; if we used 1000 we should have $\frac{1}{10}$ the effect, or, the effect is inversely as the number of times 100 grams actually used. We use G grams, therefore, $\Delta = K\frac{g}{m}\frac{100}{G}$, a formula applicable to any quantity of solvent or solute. Transposing, we get $m = K\frac{100\,g}{G\Delta}$, the actual formula in constant use for the determination of molecular weights by the boiling-point method.

From the formula it is evident that we have to determine experimentally, G (grams solvent), g (grams solute), and Δ (the raising of the boiling point). There is no difficulty in determining the weights, and our accuracy is then dependent on our thermometer, which is the most important part of the apparatus.

Beckmann's Thermometer. We have to measure small differences in temperature as accurately as possible, but it is not necessary

to know the actual temperature and the range need not be large. The Beckmann thermometer was devised for this particular purpose. It is shown in Fig. 48. The bulb contains a large amount of mercury and the capillary is fine, thus a length of about 4 cm. is secured on the scale for one degree. The whole scale comprises only five or six degrees. Each degree is divided directly into 100 parts and with the assistance of a lens it is customary to estimate tenths of the smallest division, thus expressing the readings to the thousandth of a degree.

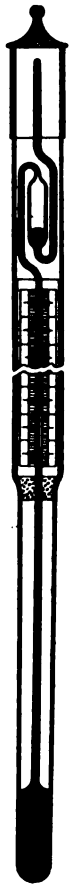


Fig. 48.

"Setting" the Thermometer. In order that one and the same instrument may be used at different temperatures there is a reservoir for superfluous mercury at the top of the capillary as shown. If the instrument is to be used to determine the increase in boiling point of water upon addition of some solute, the bulb is immersed in boiling water. The expansion drives mercury over into this reservoir. The thermometer is taken out and quickly inverted when yet more mercury flows over. It is then turned upright and by tapping sharply with the side of the finger the mercury thread is broken at the entrance to the reservoir. The excess mercury falls to the bottom and the rest subsides into the bulb. The thermometer is again put in the boiling water. If the top of the mercury column comes to rest on the scale near the bottom, the thermometer is "set" and ready for use. If it comes to rest near the top, there is still too much mercury in the bulb, for we purpose to measure ascending temperatures, and more mercury must be got over into the reservoir by repetition of the previous manipulation. If it comes to rest below the bottom of the scale we need more mercury in the bulb. We invert the thermometer and tap it gently on the table top until the mercury in the reservoir joins the thread in the capillary, and then, bringing it into an upright position, as much mercury as we please may be drawn over to the bulb. When we think we have enough, with a sharp tap we break the thread as before. Sometimes these operations have to be repeated a number of times before the mercury stands where we want it. The capacities of bulb and reservoir are so adjusted that the same thermometer may be set for any temperature through a range of 200° or more.

The Boiling-point Method. The apparatus devised by Beckmann, and still one of the best forms, is shown in Fig. 49. The vessel *A*, the size of a large test tube, has a side arm to which a return-flow condenser is attached. It contains a weighed amount of the pure solvent (about 30 g.) and the bulb of a Beckmann thermometer is immersed in the liquid. It is the temperature of the liquid, not the vapor, we must know. It also contains glass beads to a depth of 2 to 4 cm. The heating is from below and these beads break up ascending bubbles of vapor and make the temperature more uniform and constant. This experimental tube is surrounded by a cylindrical vessel of glass or porcelain, also with a return-flow condenser. This contains some of the solvent which, boiling, surrounds the experiment with a mantle of about the same temperature and minimizes variations due to drafts of air. Various devices in the way of asbestos boxes with chimneys are used as stands, heated by bunsen burners at diagonally opposite corners, the whole purpose being to render the heating as constant as possible. It is by no means easy to secure a constancy within one or two thousandths of a degree, as is quickly learned in the laboratory.

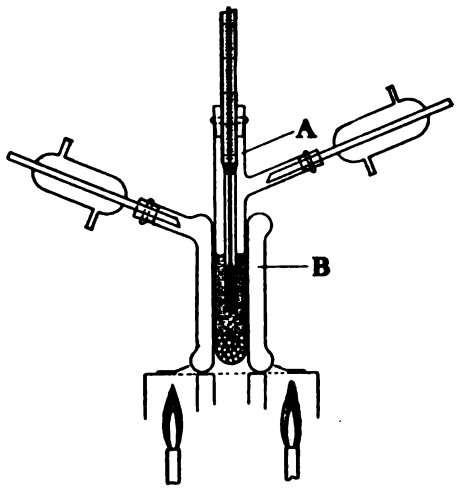


Fig. 49.

When the boiling has become reasonably vigorous and even, the thermometer (previously set for the chosen solvent) is read. After two or three minutes it is read again. Only when readings are constant to within $\frac{2}{1000}$ of a degree should the experiment be continued. This first reading of the thermometer is the most important of all, for it enters into every subsequent calculation.

If the substance whose molecular weight is sought is a solid, it is convenient to make it into pellets, the size of small lozenges, with a tablet machine. Put a number of these in a tube and weigh the whole. Drop one or two down the condenser into the boiling solvent.

Weigh the tube, and the loss in weight is the weight of substance added, g. If the substance is a liquid a quantity of it may be weighed in a pycnometer, as shown in Fig. 19. A small quantity may be put down the condenser by blowing in one end of the pycnometer and the loss in weight of the pycnometer is the weight of substance added, g.

The temperature rises and when it has become constant the second reading of the thermometer is taken. The mercury may stick and it is desirable to tap the thermometer gently but sharply before each reading. The difference between the first and second readings is the elevation of the boiling point, Δ, due to the presence of g grams solute in G grams solvent. If we know the molecular raising of the boiling point for this solvent we have only to insert these values in the formula and calculate the molecular weight of the solute.

We always make several successive additions of solute (from 3 to 7), reading the thermometer after each addition. In the calculation, g is of course always the sum of all the additions and Δ is always the difference between the first and last reading of the thermometer.

Other Forms of Apparatus. Numerous other forms of apparatus have been devised. The writer has obtained good results with a compact arrangement illustrated in Fig. 50. A Dewar vacuum-jacketed tube serves to insulate the experiment. The boiling vessel is the same that is used in Beckmann's apparatus. The heating is produced by an electric current passed through a short coil of platinum wire attached to stout wires leading to terminals, as shown. Glass beads are superfluous as fine bubbles form on the hot wire preventing any superheating, and the heating is necessarily uniform.

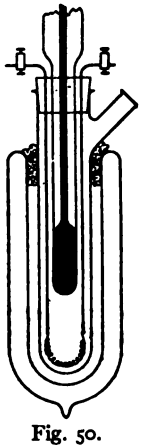


Fig. 50.

Precautions and Sources of Error. It is difficult to heat uniformly, for the gas pressure may vary or drafts may affect the flame or flames. The heat must be so applied that ebullition is lively and regular, or else it is practically impossible to obtain constant readings of the thermometer.

If a hygroscopic solvent is used, it must be protected from the moisture in the air by calcium chloride tubes in the ends of the condensers.

The barometer must be read just before and after a series of determinations, for small changes in pressure make differences in boil-

ing points readily detected with a Beckmann thermometer. For instance, water boils at 100° under a pressure of 760 mm., at 99.963° under 759 mm., and at 99.996° at 759.9 mm. A change of $\frac{1}{10}$ mm. in the pressure makes a difference of 0.004° and we read our thermometer to 0.001°. If much change is found to have occurred in the atmospheric pressure it is usually easier to repeat the work at some more auspicious time than to attempt to apply corrections.

The vapor which comes from the boiling solution must be pure solvent. If it is not, the vapor pressure of the solute is not negligible and the laws at the base of the whole method do not apply. There is little danger of error from this cause if the boiling point of the solute is 150° higher than that of the solvent.

Some solvent exists as vapor in the upper part of the experimental vessel and in the condenser, and so the solution is in fact more concentrated than we calculate from the weights.

The thermometer bulb contains less mercury at, say, 100° than at 0°. So an increase of one degree as read at about 100° is more than one degree in reality. The following table shows the magnitude of the error thus brought in, and may be used to make approximate corrections. It applies to a thermometer which is right at 15°, and one degree read on the thermometer is in fact the value given in this table.*

Temp. −35° to −30°	0° to +5°	45° to 50°	95° to 100°
0.977	0.995	1.015	1.032
Temp. 145° to 150°	195° to 200°	245° to 250°	
1.045	1.053	1.055	

Because of this error the observed Δ in most boiling-point work is then too small. This has the effect that the molecular weight calculated without this correction is too large, since Δ is in the denominator of the formula.

The laws on which the formula is based hold the better the more dilute the solution. We should then expect the best results at what we call infinite dilution, when there is nothing in solution and no raising of the boiling point. Of course we cannot measure under such conditions, but we can estimate by a process of extrapolation. In Fig. 51 successive values of Δ from one set of observations are

* Grützmacher, *Zeitschr. f. Instrumentenkunde*, 16, 202. (1896). Also Beckmann, *Zeitschr. f. phys. Chem.*, 21, 252 (1896).

laid off on the horizontal against the corresponding calculated molecular weights laid off on the vertical. The curve so determined is produced until it cuts the vertical. This corresponds to the value o for Δ and to nothing in solution. The molecular weight, *OA*, so estimated, is usually nearer the theoretical value than any of the actual determinations.

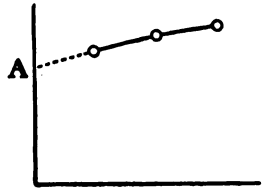


Fig. 51.

Discussion of Sources of Error. Some of these sources of error tend to increase, while others tend to decrease the numerical value of the results, and so they offset each other to a certain extent. Approximate results are usually good enough because the main use for the method is the same as that for the vapor density methods, namely, to choose one formula out of a series developed from analysis.

Illustration. The following tabulated report of an experiment will serve to illustrate some of these statements.

Solvent, benzene, K = 26.7°.
Substance, phenyl benzoate, $C_6H_5COOC_6H_5$ (198).

G	*g*	Δ	*m*	Error in per cent.
33.38	0.5041	0.195	207	+4.5
	1.0146	0.387	210	+6.1
	2.0083	0.746	215	+8.6
	3.0871	1.132	218	+10.1
	At extreme (infinite) dilution		203	+2.5

Atmospheric pressure = 751.0 to 751.5 mm.

Landsberger-Walker-Lumsden Method. Landsberger* first described, and Walker and Lumsden† soon thereafter improved, a method which is convenient if maximum accuracy is not required, if it is desired only to pick out one from a series of possible multiples of an empirical formula.

The apparatus is shown in Fig. 52. About 10 cm^3 of the pure solvent is put in the graduated tube *A*. Pure solvent is boiled in the flask *B* and the vapor is led to the bottom of *A* through the tube *C*. There condensing its heat of vaporization is liberated and heats the

* *Berichte d. d. chem. Ges.*, 31, 458–473 (1898).
† *Jour. Chem. Soc.* (London), 73, 502–511 (1898).

contents of *A*. When these have reached the boiling point the uncondensed vapor escapes through holes in the upper part of *A* and fills the larger vessel *D*, thus surrounding the experiment with a jacket of vapor at the boiling point. Excess vapor passes through *E* to a condenser. *A* contains a thermometer which need not be a "Beckmann." One graduated in tenths of a degree, upon which hundredths may be estimated by aid of a lens, is good enough for most work. After vapor has been so passed for a few minutes the thermometer ceases to rise and its reading is the boiling point of the pure solvent.

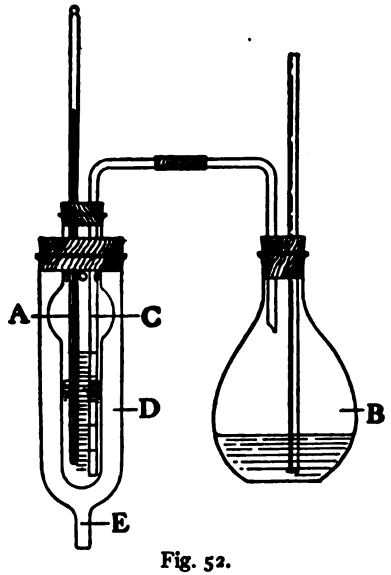


Fig. 52.

All but about 7 cm^3 of the solvent is then poured out of *A* and a weighed quantity (*g* grams) of the solute is added. The vapor is again passed through and again the contents of *A* are heated to the boiling point. This is, of course, higher than the boiling point of the pure solvent, and the increase is read on the thermometer giving the value of Δ.

It may at first appear odd that the vapor from the boiling pure solvent can raise the solution to a higher temperature, but there is nothing peculiar about it. The vapor is at a concentration such that it is in equilibrium with pure liquid solvent, and this concentration is too great to be in equilibrium with the solution at the same temperature. Therefore some vapor must condense, but in so doing the liberated heat of vaporization raises the temperature of the solution more and more. Since vapor is incessantly supplied at that particular concentration, condensation must continue until the temperature of the solution is such that its vapor pressure is the same as the pressure of the vapor coming from the flask *B*.

Having determined the boiling point of the solution we may interrupt the experiment and weigh the solution in *A*. Subtracting the weight of the solute added, *g*, we have the weight of solvent, *G*, and may substitute in our formula, $m = K\frac{100\,g}{G\Delta}$, and calculate the

molecular weight. This is Landsberger's method. Walker and Lumsden do not weigh the solution, but read its volume from the graduations on the tube A. If we know the density, d, of the solvent at its boiling point, *i.e.*, the weight in grams of one cm^3, and if we have read the volume, v, then $dv = G$, the value to be inserted in the formula.

Measuring the volume is not so accurate as weighing, but it suffices for many purposes and has the further advantage that a series of additions of solute may be made, and corresponding elevations of the boiling point determined in one experiment.

Menzies' Method. A. W. C. Menzies* has devised a method for molecular weight determinations which is accurate, rapid, and requires no thermometer at all, measuring directly the lowering of the vapor pressure due to the presence of the solute.

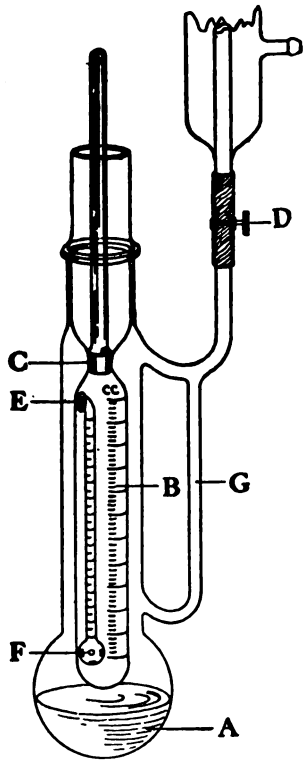


Fig. 53.

Menzies' apparatus is shown in Fig. 53. Pure solvent is put in the bulb of the outer jacket A and about 30 cm^3 is also put in the inner tube B which is graduated in cm^3. The stopper C is removed, the pinchcock D is closed, thus shutting off connection with the reflux condenser, and the solvent in A is boiled. The vapor must pass into the orifice E, down through a small tube graduated in millimeters, and out through the openings F. It then bubbles through the solvent in B and finally escapes. By this boiling-out process the solvent is freed from dissolved gases and all air is driven out of the whole apparatus. The stopper C is then put in place and the pinchcock D is opened while the boiling continues. The liquid falling from the condenser passes through the side tube G thus not cooling any part of the tube B. The solvent in B ceases to boil, but it is at its boiling point and in equilibrium with the pure vapor above it. Therefore the liquid stands at the same level in the tube B and in the tube EF.

* *Jour. Am. Chem. Soc.*, **32**, 1615–1624 (1910).

A weighed quantity (g grams) of solute is introduced into B and the blowing-through process is repeated to remove all air. Then the stopper C is inserted again and the pinchcock D is opened. In about ten minutes equilibrium is reached. But now, inside the tube B we have a solution at the boiling point of the pure solvent in equilibrium with pure solvent as vapor. The vapor pressure of the solution being less than that of the pure solvent at the same temperature, the concentration of the vapor within B is less than the concentration of the vapor in the mantle A. The pressure is proportional to the concentration, therefore the pressure in B is less and the liquid stands higher in B than it does in the tube EF. This difference in level we read on the millimeter scale carried by the tube EF and so have a direct measure of the lowering of the vapor pressure due to the presence of the solute. We must know the density of the liquid at the temperature of the observation, and then can convert the measured liquid height to the corresponding number of millimeters of mercury. To determine the quantity G of solvent present, we might weigh the liquid, but it is sufficiently accurate to read its volume from the graduations on the tube B and multiply by the density.

We now have all the data necessary to substitute in our fundamental formula, $\frac{p-p'}{p} = \frac{n}{N+n} = \frac{gM}{Gm+gM}$. The vapor pressure of the pure solvent p is, of course, the barometric pressure during the experiment. p' is the vapor pressure of the solution, and the difference, $p - p'$, is the quantity we have directly measured. We know g, the number of grams solute we added, and G, the number of grams solvent present. If we know M, the molecular weight of the solvent, m, the molecular weight of the solute, is the only unknown.

The beauty of the method lies in the fact that it gives a direct measure of the lowering of the vapor pressure and enables us to apply our fundamental formula. Of course, in practice, the calculation may be much simplified. As we determined the constant we called the molecular raising of the boiling point for each solvent, so may we determine another constant, the molecular lowering of the vapor pressure; for instance, the lowering which would be produced if we had a molecular weight of the solute present in 100 grams of the solvent. If we denote this by K' we may write $\frac{p-p'}{K'} = \frac{g\ 100}{mG}$ or $m = K'\frac{100\ g}{G(p-p')}$, a formula corresponding to that with which we are already familiar.

Menzies* has also called attention to the fact that his apparatus may be used to determine molecular weights on the principle of the Bleier-and-Kohn method described in Chapter XII.

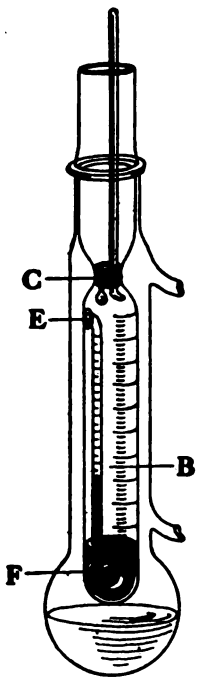


Fig. 54.

A weighed quantity of the liquid to be investigated, sealed in a bulb as for the Hofmann, Victor Meyer, or Bleier-and-Kohn method, is attached to the under side of a rubber stopper by inserting the capillary in a shallow cut as indicated in Fig. 54. A glass rod passes through the stopper and is bent in such a way that when it is turned it will break the bulb. Mercury is put in tube *B* and some liquid is boiled in the outer mantle until the whole apparatus reaches a constant temperature. Then the rubber stopper, carrying the bulb and rod, is inserted, and when the temperature has again become constant the bulb is broken. The increased pressure in *B*, due to the vaporization of the substance, causes the mercury to rise in the tube *EF*. This increase in pressure is measured by the difference in level of the mercury in *B* and in *EF*. We may determine the constant for the apparatus, *i.e.*, the increase in pressure which would be produced if we had vaporized a molecular weight in grams in that tube at that temperature. Call this *c*. If the actually observed increase be denoted by Δ, then $\frac{\Delta}{c} = \frac{g}{m}$, the same formula used for the Bleier-and-Kohn method.

Using Menzies' apparatus no hot air is driven to a cooler place, and in this respect it is superior to Bleier and Kohn's device. But on the other hand we cannot work under diminished pressure, and the temperature range is more limited, for we must use glass and mercury.

Measurement of Electrolytic Dissociation by the Boiling-point Method. Electrolytes in water give too small molecular weights. The plausible explanation for this is that they are dissociated into their ions.

The method by which we calculate the degree of dissociation from the raising of the boiling point is almost identical with the method we used for calculating the degree of gaseous dissociation from a de-

* *Jour. Am. Chem. Soc.*, **32**, 1624–1628 (1910).

termination of the vapor density. But there is an inversion in the proportion which might trip one unless attention were called to it.

Suppose that we know the molecular weight and the number of ions resulting from the dissociation of one molecule. Call this number n. If there were no dissociation we should get a raising of the boiling point, δ. We calculate the value of δ by substitution in the boiling-point formula, $\delta = K \frac{100\, g}{G m}$. We observe a raising of the boiling point Δ, greater than δ. Let γ = fraction dissociated; then $1 - \gamma$ = fraction not dissociated. Start with 100 molecules, and we have $100\,\gamma n$ due to dissociation and $100\,(1 - \gamma)$ not dissociated, or a total of $100\,\gamma n + 100\,(1 - \gamma)$.

The greater the number of molecules the greater the raising of the boiling point. Therefore we may write the proportion,

$$100 : 100\,\gamma n + 100\,(1 - \gamma) = \delta : \Delta.$$

Notice that this is a direct proportion, while in calculating the degree of gaseous dissociation from the vapor density we have an inverse proportion. Solving for γ we get $\gamma = \frac{\Delta - \delta}{\delta\,(n - 1)}$.

In some solutions association probably takes place; for instance, 10 per cent acetanilide in benzene appears to exist as double molecules.

Freezing-point Method. The lowering of the freezing point, due to the presence of a dissolved substance, like the boiling point, is directly proportional to the lowering of the vapor pressure. Pure solid solvent crystallizes out at the temperature at which the vapor pressures of solid and solution are the same. The proportionality is shown in Fig. 55. A is the vapor-pressure curve for the pure solvent, B for a solution containing x solute, and C for a solution containing y solute. DE is the vapor-pressure curve of the solid pure solvent. Then a, b, and c are the melting points. The distances ab and ac on the horizontal are the lowerings of the freezing point, the distances Db' and Dc' on the vertical are the lowerings of the vapor pressure. If the solutions are dilute the curves are nearly parallel and so, having to do with similar triangles, $ab : Db' = ac : Dc'$ or the

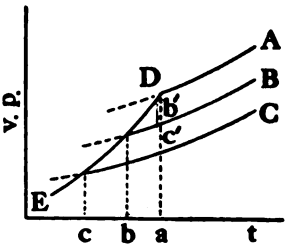


Fig. 55.

lowerings of the freezing point are proportional to the lowerings of the vapor pressure.

The principles being the same as those of the boiling-point method, the formula is the same, $m = K\frac{100\,g}{G\Delta}$, the only difference being that Δ here is the lowering of the freezing point instead of the raising of the boiling point, and K is the molecular lowering of the freezing point instead of the molecular raising of the boiling point. It is the lowering produced when one molecular weight in grams of a solute is dissolved in 100 grams of the solvent. It is, of course, numerically different from the molecular raising of the boiling point for the same solvent.

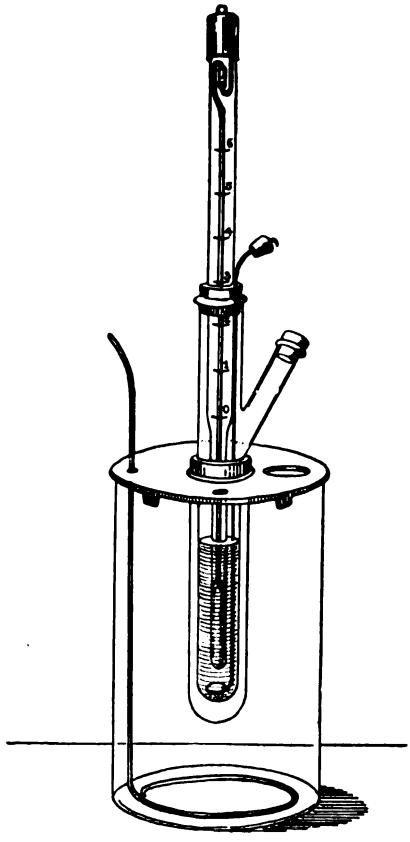


Fig. 56.

The same thermometer is used in both methods, only in preparing to use it for the freezing-point method, it is set in such a way that the mercury comes to rest near the top of the scale when immersed in melting pure solvent. This is because subsequent readings will be lower and lower.

The Apparatus. The apparatus is shown in Fig. 56. It consists of an inner vessel, the same used in the boiling-point method, to contain the experiment; a slightly larger tube serving as a jacket to prevent direct contact between the experimental vessel and the cooling bath; a battery jar to hold the cooling bath, and ring-form stirrers in experiment and bath.

Determining the Freezing Point. A cooling bath is prepared having a temperature from 4° to 6° below the freezing point of the

pure solvent. A weighed quantity (about 30 g.) of pure solvent is put in the experimental vessel and this is inserted directly into the cooling bath to save time. The stirring, produced by up-and-down motion of the ring stirrer, must be continuous and regular.* The mercury in the thermometer should be watched, not the liquid in the vessel. It falls too far, owing to a supercooling, and then starts to rise, owing to the evolution of the heat of fusion as the liquid freezes. The moment this upward movement begins, the experimental vessel is taken out of the cooling bath, wiped quickly, and put into the jacket tube. Stirring must not be interrupted more than is absolutely necessary. The mercury will continue to rise for a time and then come to rest, for perhaps a minute, at some definite point, after which it is apt to move again. This point at which it stays for a brief time is the freezing point sought.

Some Supercooling Necessary. Some supercooling is essential to the method in order that we may note this fall, followed by the rise to a temporarily stationary position, but too much supercooling is a source of error. If our solvent does not give us enough supercooling, it is hard to remedy the fault. If it has a tendency to give us too much, we may " vaccinate " with a particle of the solid. The moment that a particle of the solid phase is inserted in the experiment, the metastable equilibrium cannot continue and the temperature rises while ice separates out.

Having read the freezing point on the empirical scale the ice should be melted and the whole experiment should be repeated. Successive observations should agree to within 0.002° before proceeding with the experiment, for this first determination is the most important of all.

Additions of Solute. The solute is weighed as pellets in a tube if solid, or in a pycnometer if a liquid, as in the boiling-point method. A small quantity is inserted through the side arm, completely dissolved, and the new, lower melting point determined as described. The difference between the two melting points is our Δ, and knowing G, g, and K we substitute in the formula and calculate the molecular weight.

A series of determinations after the addition of successive portions of a substance is always made, and the Δ is always the difference be-

* Electrically actuated stirring is desirable. The platinum ring stirrer is attached to an iron ring above. A metronome makes and breaks a circuit through an electromagnet outside. Thus the stirrer rises and falls with regularity and, the vessel being completely closed, hygroscopic solvents may be used.

tween the first and the last freezing points, and g is always the sum of all additions.

It is well to plot the results and estimate the value for "infinite" dilution as described for the boiling-point method.

Precautions and Sources of Error. The laws apply best to most dilute solutions and the greater the concentration the greater the probability of error.

The ice which separates out must be pure solvent, otherwise the results are worthless. If solvent and solute are isomorphous they may crystallize out together as mixed crystals. Iodine dissolved in benzene and thiophene in benzene are illustrations of this behavior.

The ice which separates out diminishes the amount of solvent and the solution becomes more concentrated. It is possible to apply a correction for this, determined from the amount of supercooling. For example, suppose we have 25 grams of water as the solvent and that we observe one degree of supercooling. Then the amount of ice which separated out was sufficient to liberate 25 cals., for this amount of heat was required to raise the temperature of the whole experiment to the true freezing point. The heat of liquefaction of ice is 80. Therefore $\frac{25}{80}$ gram of ice formed, and this weight is to be subtracted from the weight of solvent used.

The same error occurs in this method as in the boiling-point method due to the different amounts of mercury in the bulb of the thermometer at different temperatures. The table showing the amount of this correction was given in the discussion of the boiling-point method.

The greatest variations in atmospheric pressure which are at all likely to take place produce so slight an effect upon the freezing point that they may be neglected.

Electrolytes in water as a solvent have too great an effect on the freezing point. The molecular weights come out too low. We assume these substances to be dissociated into their ions. The results by the freezing-point method may be utilized to determine the degree of dissociation in exactly the same way as the results by the boiling-point method.

In some cases our molecular weights come out too high and we assume association to more complex molecules takes place. For instance, 35 per cent ethyl alcohol in benzene as the solvent gives us results seven or eight times the generally accepted molecular weight of alcohol.

Freezing-point Method Applicable to Substances with High Melting Points. The freezing-point method is applicable to substances which freeze at high temperatures. When such a substance is used as a solvent we merely substitute a correspondingly hot bath for the more usual freezing mixture. For instance, the method is applicable to the determination of molecular weights of metals dissolved in other metals.

Molten metals behave like other more familiar liquids. Liquid tin and lead are miscible in all proportions like alcohol and water; liquid zinc and lead form two layers, each containing a little of the other, like ether and water. Molecular weight determinations with molten metals as solvents are not entirely satisfactory. The greatest difficulty is the marked tendency which metals have to freeze together, so that the "ice" which separates out is very seldom pure solvent.

As far as they go and in a general way, such results indicate that metals in dilute solution in other metals are "monatomic."*

Lowering of Vapor Pressure and Osmotic Pressure. The osmotic pressure of dilute solutions has been shown to be proportional to the concentration of the solute. The lowering of the vapor pressure of dilute solutions also has been shown to be proportional to the concentration of the solute. Since they are proportional to the same thing they must be proportional to each other. Therefore any method of measuring the lowering of the vapor pressure is an indirect method of measuring osmotic pressure, and this is why the boiling- and freezing-point methods are called the indirect osmotic methods.

This is a simple statement of self-evident facts and is entirely free from any hypothesis as to the cause of osmotic pressure. It does not even state that there is a causal connection between the two. We should not say that osmotic pressure produces lowering of the vapor pressure, nor that lowering of the vapor pressure causes osmotic pressure. These are coincident phenomena probably due to the same cause which we do not well understand.

There is no causal sequence here but simultaneous phenomena and various devices have been imagined to make clear that they measure the same thing. The most convincing of these is a machine suggested by van't Hoff. Suppose we have a cylinder with a piston consisting of an ideally perfect semipermeable membrane. If the cylinder con-

* For additional details and full working directions see the laboratory manuals referred to at the beginning of Chapter XII.

tains pure solvent the least pressure on the piston will push it to the bottom, for it permits the passage of the solvent without hindrance. If the cylinder contains a solution, it requires pressure on the piston to hold it in position and this pressure is equal to the osmotic pressure of the dissolved substance. By applying a pressure slightly in excess of the osmotic pressure the piston may be pushed down, and this will extract pure solvent while the solute is compressed. The work done during this operation is measured by the pressure acting, multiplied by the volume through which it acts. Since the gas laws apply for dilute solutions, the gas equation $pv = RT$ applies, and it is as if we compressed a gas.

Now in the boiling-point method pure solvent goes off as a vapor and the solute is accordingly compressed; in the freezing-point method pure solvent separates out as ice and the solute is compressed. If this is not true the methods are not applicable. So in these methods we realize our ideal semipermeable membrane. The lowering of the freezing point, the raising of the boiling point, the osmotic pressure are all measures of the resistance of a solute to having its volume diminished. This leaves unanswered the question why it resists an effort to diminish its volume.

Calculation of Molecular Lowering of Freezing Point. With the assistance of this machine, and its ideally perfect semipermeable membrane for a piston, we can bring out an interesting relationship between the molecular lowering of the freezing point and the heat of fusion of the solvent.

Suppose we have, in such a cylinder, a large quantity of a solution of such concentration that each 100 grams solvent contains a molecular weight in grams of solute. It is in a much larger tank to hold the temperature constant at T_0, the freezing point of the pure solvent. We push the piston in against the osmotic pressure until we have extracted 100 grams solvent. Owing to the large quantity of solution present we may neglect the increase in pressure required as the volume diminishes. In this operation we have then done work equal to pv. We now allow the extracted solvent to freeze. Its heat of fusion is ρ, and so we obtain 100ρ calories in this operation. We next bring the whole apparatus to the lower temperature, the freezing point of the solution. If K is the lowering of the freezing point due to the presence of a molecular weight in grams of solute in 100 grams solvent, this lower temperature is $T_0 - K$. We bring solution and ice into contact and allow the ice to melt, in which process it takes

up 100 ρ calories. We now bring the whole back to the original conditions and have completed a cyclical process.

For such a process the equation holds, $dA = Q\frac{dT}{T}$ (see equation (6), Chapter XXII). We transferred the total quantity of heat 100 ρ cal. i.e. Q through the temperature interval K, i.e. dT, and did work pv, i.e. dA. Substituting we have, $pv = 100\,\rho\,\frac{K}{T}$. Now $pv = RT$, and where we have to deal with a molecular weight in grams, as in this case (for a molecular weight in grams was dissolved in 100 g. of the solvent), $R = 1.98$ cal. Therefore,

$$1.98\,T_0 = 100\,\rho\frac{K}{T_0}, \text{ or, } K = \frac{0.0198\,T_0^2}{\rho}.$$

The following table shows how closely the experimental facts correspond to this deduction:

	T_0	K experimental.	ρ	$\frac{0.0198\,T_0^2}{\rho}$.
Water	273	18.5	79.15	18.65
Acetic acid	290	39	43.66	38.15
Benzene	278.5	51.2	30.08	51.06
Naphthalene	353.1	68	35.5	69.55
Nitrobenzene	278.3	70.5	22.3	68.77
Phenol	311.5	74	24.93	77.09

It is evident enough we may use this formula either way about, if we know the heat of fusion to calculate K, if we know K to calculate the heat of fusion, with a fair degree of accuracy.

Calculation of Molecular Raising of Boiling Point. Similar reasoning leads to the same formula connecting the molecular raising of the boiling point with the heat of vaporization, as follows:

Suppose we have in our cylinder with an ideal semipermeable piston a solution containing a molecular weight in grams of a solute in each 100 g. solvent. At the boiling point of the solvent, T_1, we push in the piston until we have extracted 100 g. pure solvent. We thus do work equal to pv. We allow the solvent to vaporize and so doing add 100 λ cals. (λ = heat of vaporization.) We raise the temperature to the boiling point of the solution, $T_1 + K$, and allow the vaporized solvent to condense. This liberates 100 λ cals. We cool the whole to T_1 again and are at the starting point. Total heat trans-

ferred is 100λ cals. and work done is pv. Therefore, substituting in the equation $dA = Q\frac{dT}{T}$ as before, we have $0.0198\,T_1 = 100\lambda\frac{K}{T_1}$, or $K = \frac{0.0198\,T_1^2}{\lambda}$.

The following table shows how well this deduction accords with the facts:

	T_1	K experimental.	λ	$\frac{0.0198\,T_1^2}{\lambda}$.
Water	373	5.2	541	5.09
Sulphur dioxide	263	15	91.8	14.92
Chloroform	334.2	36.6	58.5	37.80
Acetone	329.3	16.7	125.3	17.14
Benzene	353.3	27.3	93.45	26.46
Aniline	457	32.2	93.3	44.32

This formula enables us to calculate the heat of vaporization from the molecular raising of the boiling point or the molecular raising of the boiling point from the heat of vaporization.

CHAPTER XXIV

THE PROCESS OF SOLUTION AND PRECIPITATION

IT is a matter of daily experience that certain substances will dissolve in certain solvents readily, forming more or less concentrated solutions, and that others are practically insoluble. Why a given substance should dissolve in one solvent and not in another, why anything dissolves at all, we do not know, any more than we know why certain substances react chemically and others do not. But we have observed and recorded many experimental facts and have formulated a number of generalizations which are of much value.

Solution Pressure. A substance has a tendency to dissolve. This is, in many ways, analogous to the vapor pressures which all substances have and so we speak of a substance as having a "solution pressure."

Solubility. We express the solubility of a substance in terms of concentration. The amount in grams per liter or formula weights per liter (or any other convenient set of units), which will go into solution at a definite temperature, is a constant. A solution which has taken up all the solute it will we call a saturated solution. The concentration corresponding to this condition is the solubility of the substance.

Precipitation Pressure. The substance in solution exerts an osmotic pressure and we may consider this as, in a sense, a measure of the tendency of a substance to come out of solution or to precipitate. With the aid of this conception we may imagine a saturated solution in contact with excess solute as in a condition of equilibrium, in which the quantity which dissolves per unit time, owing to solution pressure, is just equaled by the quantity which separates out per unit time, owing to what may be called the precipitation pressure.

The Solution of Gases. Different gases are differently soluble in a given liquid. The concentration of a saturated solution depends on the natures of solvent and solute, on the temperature and on the pressure. It is a general rule, without any exception, that the higher the temperature the less the solubility of a gas.

Henry's Law. If we exhaust the air from above water containing dissolved air, the latter soon appears as minute bubbles, some of which collect on the sides of the vessel, while some rise through the body of the liquid. The amount of a gas which a liquid will dissolve is directly proportional to the pressure. That is, if we double the pressure, we double the amount dissolved. This is Henry's law, first announced in 1803. It applies only when the gas may be considered as not uniting chemically with the solvent. It does not apply to such gases as hydrogen chloride or ammonia, which are extremely soluble; nor even to such a gas as carbon dioxide, which is relatively soluble; but it does apply to such gases as nitrogen, hydrogen, oxygen, carbon monoxide, and methane.

Formulation of Henry's Law. If C_1 represents the concentration of the gas in the liquid phase, and C_2 the concentration of the gas in the gaseous phase, we may express Henry's law as follows: $\frac{C_1}{C_2} = K$, where K is a constant. This equation holds no matter how we vary the pressure, provided the temperature is constant. At first, this sounds paradoxical, but consider, when we double the pressure we double the concentration in the gaseous phase, and this is followed by a doubling of the concentration in the liquid phase. This is exactly what Henry's law states will occur and so the equation is a particularly satisfactory form in which to express the law.

Coefficient of Solubility. This "K," or ratio between the concentrations in the two phases, is known as the coefficient of solubility, or solubility coefficient.

Bunsen's Coefficient of Absorption. Bunsen, who did much work upon the solubility of gases in liquids, expressed his results somewhat differently. He determined experimentally the volume of the gas which dissolved in 1 cm^3 of the liquid at a given temperature, the gas exerting a pressure of 760 mm. He then applied the gas laws and reduced this found volume to normal conditions, i.e., to 0°, and this calculated volume is what is called the coefficient of absorption.

Some Absorption Coefficients. The absorption coefficients of such gases as nitrogen, hydrogen, and oxygen are of the same order of magnitude, and vary from 0.02 to 0.05. The absorption coefficients of such gases as carbon dioxide and hydrogen sulphide vary between 1 and 4; those of ammonia and hydrogen chloride are much higher.

Oxygen	0°	0.04890	Hydrogen Sulphide	0°	4.686
Oxygen	20°	0.03102		20°	2.672
Hydrogen	0°	0.02153	Ammonia	0°	1298.9
Hydrogen	20°	0.01837	Ammonia	20°	710.6
Nitrogen	0°	0.02388	Hydrogen Chloride	0°	506.5
Nitrogen	20°	0.01639		20°	442.0
Carbon Dioxide	0°	1.713	Acetylene	0°	1.73
	20°	0.878	Acetylene	20°	1.03

Dalton's Extension of Henry's Law. The individual gases of a mixture dissolve according to their partial pressures and the solubility of each is but slightly affected by the presence of the other. For instance, air is a mixture, and as four-fifths of the barometric pressure is due to nitrogen and one-fifth to oxygen, the quantity of nitrogen which dissolves in unit volume of water from the air is just four-fifths of what would dissolve were the air pure nitrogen. The quantity of oxygen which dissolves in a given volume of water is just one-fifth of what would dissolve were the air pure oxygen. This is known as Dalton's extension of Henry's law.

Illustrations of Henry's Law. The pressure of carbon dioxide in a bottle of charged water is large. Pull the cork, relieving the pressure, and the dissolved gas promptly "precipitates" and we have the familiar phenomenon of effervescence.

In a factory a large siphon was used to convey cold water from one tank to another, and much difficulty was experienced because the siphon stopped running every now and then. When this occurred, the highest portion of the bend was found to be filled with air. Henry's law offers the explanation for this phenomenon. Under atmospheric pressure air dissolved in the water. When the water reached the higher portion of the siphon it was under a lower pressure, and then of course some dissolved air came out and collecting at that place stopped the action of the siphon.

Run a current of pure air through water containing carbon dioxide and the carbon dioxide may be swept out completely, for the partial pressure of the carbon dioxide in the gaseous phase is thus held down to a vanishingly small quantity. In general, one gas may be so driven out by another and this is a particularly convenient and expeditious method to remove any volatile substance from a solution. Distillations with steam, in which steam is forced through a solution or a pure substance, are but slightly different applications of the same principles.

The Solution of Liquids. Some liquids are mutually soluble in all proportions, and we call such liquids completely miscible. Others are mutually soluble to definite amounts only. Ether and water are not miscible in all proportions, but water dissolves some ether and ether dissolves some water. There is no such thing as absolute insolubility. Theoretically, at least, everything is soluble to a certain extent in everything else.

Influence of Temperature. The effect of a change in temperature on the mutual solubility of two liquids is not always the same. Raising the temperature, ether becomes less soluble in water, but water becomes more soluble in ether.

The Critical Point of Solubility. Suppose that we have some phenol and water in a test tube. At ordinary temperatures there will be two layers, the lower being a saturated solution of water in phenol, the upper a saturated solution of phenol in water. The two layers constitute two phases separated by a bounding surface, a meniscus. This meniscus is due to the surface tension which exists between the two liquids.

Upon raising the temperature, this meniscus becomes flatter and disappears entirely at 70°. At this temperature, then, there is no surface tension between the two liquids, and they are miscible in all proportions. By a "critical" point we mean one at which two phases which are approaching identity become one; a point where a diminishing surface tension becomes zero, where a meniscus or surface dividing two phases vanishes. Therefore, this lowest temperature (70° for phenol and water) at which two liquids are mutually soluble in all proportions, is properly named the critical point of solubility.

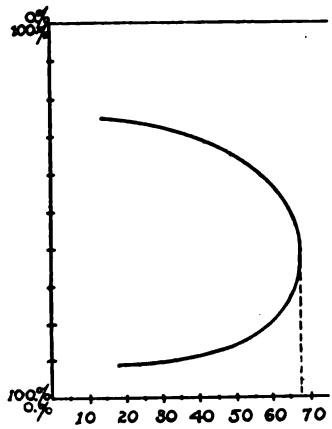


Fig. 57.

These relations are shown graphically in Fig. 57. In a coördinate system along the abscissa lay off temperature. Along the ordinate, from the origin upward, lay off per cent water in the phenol phase. On this same perpendicular downward from a second origin or abscissa, which represents 100 per cent water, lay off per cent phenol

in the water phase. Repeat this on another perpendicular corresponding to a higher temperature, and so on. In this way we obtain pairs of points which gradually approach each other. When these points are united by a curve, it has the appearance shown in the figure, bulging out to the right. A perpendicular tangent to the extreme right-hand point of this curve corresponds to the critical point of solubility. It is clear from the diagram that the two liquids are mutually soluble in all proportions at any temperature to the right of this tangent, and that we may expect two phases separated by a bounding surface at any point to the left of this tangent, and included within the interior of the curve.

Such diagrams may be drawn also for isobutyric acid and water, for salicyclic acid and water, for benzoic acid and water, etc.

We sometimes find that the mutual solubilities diminish with increasing temperature and increase with a diminution in temperature. Triethylamine and water furnish an instance of this. The diagram for these substances appears much like that of Fig. 57, only with the bulge pointing in the opposite direction. A tangent drawn to the extreme left of that curve then represents the critical point of solubility, and we see that the two liquids are mutually soluble in all proportions at any temperature below the one represented by the tangent, while at any higher temperature we may expect to have two phases separated by a bounding surface.

There must be a surface tension of less than nothing between perfectly miscible liquids such as alcohol and water. Instead of a bounding surface we must imagine a tendency to pass into each other and occupy the largest possible volume, a property which reminds us much of the behavior of gases.

General Formulation. The equation which we wrote for Henry's law is applicable to solid and to liquid solutes as well as to gases. At any given temperature the concentration of a liquid or solid is a constant, so C_2 of that equation is a constant and may be merged in the constant K, and so we have, $C_1 = K$. This is merely a simple expression of the well-known fact that a substance shows a definite solubility for any definite temperature.

An Empirical Rule Regarding Solubility. We have learned by experience that chemically similar substances are usually mutually soluble, and that chemically dissimilar substances are usually but very slightly soluble in each other. For instance, benzene is soluble in toluene and very slightly soluble in water. Benzene and ether

and other organic liquids are good solvents for organic substances, but are poor solvents for inorganic salts.

We may expect substances containing the hydroxyl group to be soluble in water. In harmony with this expectation we find the alcohols, glycerol, sugar, etc., decidedly soluble. On the other hand, there are noteworthy exceptions to this rule. For instance, the hydroxides of the metals not in the first group of the periodic system are relatively insoluble.

Conforming to the rule we find that organic acids are more soluble in water than other types of organic compounds. These acids, we assume, give hydrogen ions when dissolved in water and in so far are similar to water.

"Insoluble" Precipitates. The most "insoluble" precipitates of analytical chemistry are soluble to an extent readily measured by the conductivity method (see Chapter XXVIII).

The Change of Solubility with Change of Temperature. Solubilities of substances vary in almost every conceivable manner and degree with the temperature. As a general rule substances are more soluble the higher the temperature. The increasing solubilities of potassium nitrate and potassium bromide may be taken as typical examples. But we also know of substances which are less soluble the higher the temperature. Lithium sulphate is a good illustration of this. We also know of substances whose solubility is independent or nearly independent of temperature. Common salt is an example. Other substances show a solubility rising to a maximum, like strontium nitrate; others show an increase followed by a decrease, as calcium sulphate; others show a decrease followed by an increase, as calcium n-butyrate.

Solubility Curves. Lay off temperatures on the abscissa and concentrations of saturated solutions (expressed in any convenient units, grams solute per 100 grams solvent, or molecular weights solute per liter solvent) on the ordinate, and we obtain our much-used solubility curves. Figure 58 contains the solubility curves of the substances mentioned.

There is such an infinite variety in these phenomena that at first it seems as though no generalization were possible, and yet one of great significance has been made.

Van't Hoff's Law of Mobile Equilibrium. We always find that when solution takes place with an evolution of heat the substance is less soluble the higher the temperature, and that when solution

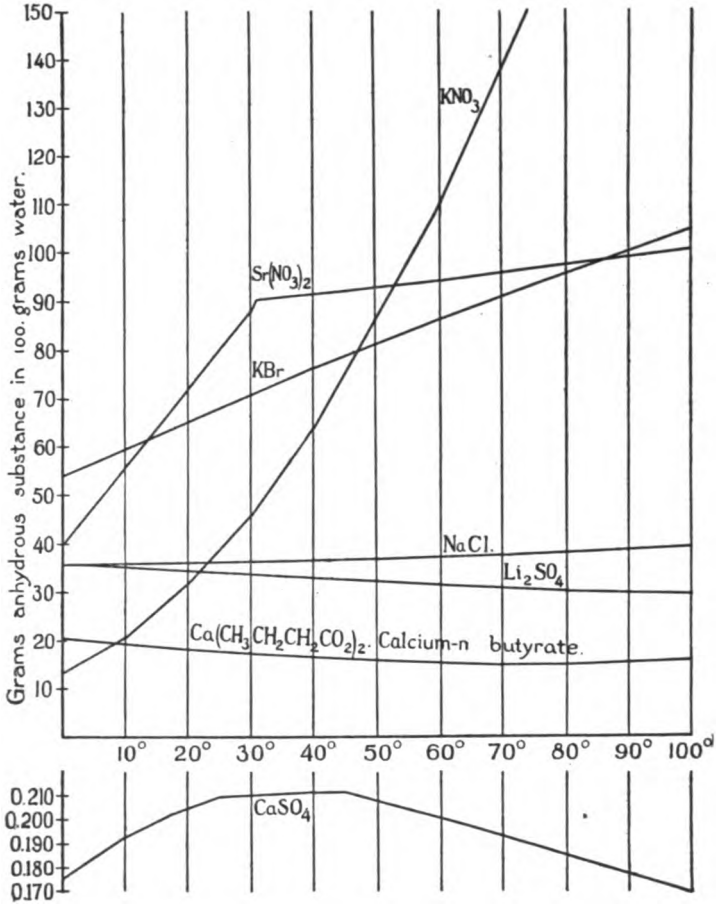


Fig. 58.

takes place with absorption of heat, the substance is more soluble the higher the temperature.

A saturated solution in contact with an excess of solid is in equilibrium. We raise the temperature and we find the equilibrium conditions alter in such a way as to absorb heat. If the solute dissolving absorbs heat, some will dissolve; if the solute precipitating absorbs heat, some will precipitate. This principle has been found to be applicable generally to conditions of equilibrium in chemical reactions as well as in processes of solution, in short to all conditions of equilibrium, both homogeneous and heterogeneous. We may say

that if we alter the temperature of a system in equilibrium, the system will alter in such a way as to minimize the temperature change. This is known as van't Hoff's law of mobile equilibrium.

The underlying idea of this law has been found to be of wide applicability and not confined to temperature changes.

The Change of Solubility with Change of Pressure. The volume of a solution is not an additive property. That is, it cannot be calculated as the sum of the volumes of the components. Generally the process of solution is accompanied by a contraction. For instance, if we half fill a tube about a meter long with water, and fill the other half with alcohol, taking care that the two liquids do not mix, cork the tube and shake it, although it is completely full at first, when the mixing has been accomplished several cubic centimeters of vapor space appear at one end. The solution of alcohol and water is accompanied by a contraction.

In a few cases solution is accompanied by an expansion. For instance, the volume of a solution of ammonium chloride in water is greater than the sum of the volumes of the components. We cannot, then, from the specific gravity, determine the amounts present, unless we have tables worked out from previous experiments. The differences between the sum of the volumes of the components and the volume of the resulting solution are greater when water is the solvent than in any other case.

Increasing the pressure on a system consisting of saturated solution in equilibrium with excess of solid has been found to cause more solid to go into solution if this process is accompanied by a diminution in volume, and to cause the precipitation of some solid if this process is accompanied by a diminution in volume. While the changes in solubility thus produced by changes in pressure are not very great for changes of one or two atmospheres yet they are easily measurable. The system alters in such a way as to minimize the pressure change if it can. Notice that this is the very same principle stated for temperature changes. This generalization regarding the effect of pressure also has been found to be universally applicable to homogeneous as well as to heterogeneous equilibria.

Le Chatelier's Law. These and all other special cases have been condensed into what we call Le Chatelier's law (often called Le Chatelier's theorem). A system in equilibrium alters in such a way as to neutralize or partly neutralize the change we are forcing upon it. Another way of stating it is: whenever we apply an external force to

any system in equilibrium the system will, if it can, alter in such a way as to diminish the effect of the applied force.

This is one of the most important and useful laws we have regarding conditions of equilibrium, for it enables us to foretell, qualitatively at least, what will happen.

Cooling Effect of Dissolving. In most instances when a salt dissolves in water we observe a cooling effect. For instance, the fall in temperature is very marked when we dissolve potassium iodide or potassium nitrate in water.

In our study of osmotic phenomena we learned that dissolved substances behave in many particulars like gases under the same conditions of temperature and pressure; that the condition of being in solution is in many ways analogous to the gaseous state. The most essential difference between a substance as solid, liquid, or gas is its energy content, and to convert a solid or liquid to a gas we must give it energy in the form of heat, the heat of fusion or of vaporization, or both. So, in dissolving, a substance must take up a quantity of heat equal to its heat of vaporization or heat of sublimation. If no heat, or not enough, is given to the system it must take it from its own internal energy. This of course results in a cooling, and so we plausibly explain the cooling effect observed to accompany the solution of most salts.

Sometimes a Heat Effect. But all substances do not absorb heat when they dissolve. On the contrary, the solution of ferric chloride or of sulphuric acid in water is accompanied by a decided evolution of heat and the temperature of the system rises.

The Analogy not Perfect. So our analogy between the process of solution and the changes between the three states of aggregation is not perfect, and the consideration of the process of solution is complicated by the coincident appearance of other phenomena, of some other form of energy which is converted into heat.

Solution in Part a Chemical Reaction. This other form cannot well be anything but chemical energy, and so we reach the conclusion that the process of solution must frequently, if not always, be in part a chemical reaction, and what we measure when we determine the quantity of heat evolved or absorbed is the resultant of these two manifestations. They must almost always be opposed to each other in their effects since almost all chemical reactions are accompanied by the evolution of heat, and changes from a more dense to a less dense condition of aggregation are always accompanied by the absorption of heat.

Not Sure what We Have in Solution. Just what the result of the chemical reaction is, whether the formation of molecular compounds between solvent and solute, or between the ions of the solute and molecules of the solvent, or something else, is a hard matter to decide; in fact, it cannot be considered as decided at the present time.

Much of what follows is a series of facts and considerations bearing on this question. These give us hints and furnish information of practical value, but do not give a final answer to the fundamental question, what have we in a solution?

The process of solution and the equilibrium conditions between saturated solution and excess solute have been a favorite theme for investigations. The quantity of information we have accumulated is vast and would require a volume at least the size of this for its presentation. We must content ourselves with a consideration of a few simple cases. But they are typical and suffice to introduce the fundamental principles, and a familiarity with them is a necessary and adequate preparation for profitable study of the more elaborate and complicated treatments to be found in more highly specialized works.

Solubility of Sodium Sulphate and its Hydrates. The most common form of sodium sulphate is " Glauber's salt " containing ten

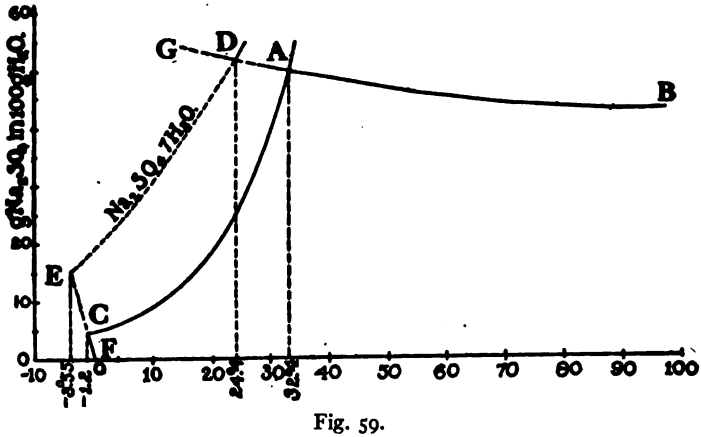


Fig. 59.

molecules of water of crystallization ($Na_2SO_4.10H_2O$), also called the decahydrate. Shake up a large excess of this with water at a definite temperature until a saturated solution is obtained. By evaporating

and weighing a sample of this saturated solution determine the number of grams of the anhydrous substance, Na_2SO_4, present per 100 grams of water. Lay off a distance corresponding to this analytical result on a vertical corresponding to the temperature. Repeat at other temperatures. In this way we obtain a series of values, which, united, give us the solubility curve *CA* in Fig. 59. This shows a rapidly increasing solubility with increasing temperature.

Transition Point at A. If we raise the temperature above 32.4° we notice a change occurs in the solid substance. The large, clear crystals become coated with a white nontransparent powder, and soon the crystals have all crumbled to a heap. Analysis shows this to be anhydrous sodium sulphate. This is then a transition point, the temperature at which solid $Na_2SO_4.10H_2O$ changes to solid Na_2SO_4.

By working carefully it is possible to pass this point without having the change occur. Our results correspond to a prolongation of the curve *CA* above *A*. The solid is then in a metastable condition, superheated above its transition point.

Solubility of the Anhydrous Salt. Successive analyses of the solution at ascending temperatures, after the transformation has occurred, show lower and lower concentrations of sodium sulphate in solution. The results plotted on the same diagram give the curve *AB*, the solubility curve for anhydrous Na_2SO_4, showing a diminishing solubility with increasing temperature.

Prolongation of Curve BA. Starting from a temperature above 32.4° with a saturated solution in contact with a large excess of solid anhydrous sodium sulphate, we may cool gradually for some distance below 32.4° without having the transformation into Glauber's salt set in, provided no particle of the decahydrate is present. Analyses of the solution give results which plotted prolong the curve *BA* through *D* toward *G*. This is still the solubility curve for the anhydrous salt, but represents, of course, conditions of metastable equilibrium.

The Heptahydrate. If we push the supercooling far enough the limits of the metastable condition are reached, a change sets in spontaneously and we observe crystals forming again. But upon analysis these crystals prove not to be the original decahydrate but a new solid, sodium sulphate with seven molecules of water of crystallization ($Na_2SO_4.7H_2O$), the heptahydrate.

Solution Pressure of the Heptahydrate. We have learned that when a metastable condition of equilibrium breaks down spontane-

ously and either one of two new forms can appear, it is a general rule that that one will appear which involves the smaller lowering of the vapor pressure. Apparently this rule applies in cases such as we are considering, with the substitution of the term solution pressure for vapor pressure. The heptahydrate evidently has a higher solution pressure than the decahydrate because it maintains itself in equilibrium with solutions containing more Na_2SO_4 than those solutions with which the decahydrate is in equilibrium at the same temperature.

Solubility of the Heptahydrate. As the temperature falls, more and more of the solid heptahydrate precipitates and determinations of the concentrations of the solutions at different temperatures give us the values which are plotted as the curve *ED*, the solubility curve for this heptahydrate. It is, at all temperatures, in a metastable condition, and the addition of the least particle of the decahydrate starts the change to the more stable Glauber's salt.

Transition of Heptahydrate to Anhydrous Sulphate. Starting anywhere on the curve *ED*, with a plentiful excess of the solid heptahydrate, and raising the temperature, at 24.4° a change occurs in the solid form, the heptahydrate loses its seven molecules of water of crystallization and becomes anhydrous. 24.4° is then another transition point, the temperature of change from the heptahydrate to the anhydrous variety.

Prolongation of Curve ED. Working carefully it is possible to obtain results corresponding to a prolongation of the curve *ED* upward beyond *D*, a metastable condition; the solid heptahydrate is then superheated above its transition point.

The Ice Curve. Pure water freezes at 0°, the point marked *F* on the abscissa in the diagram. If we dissolve a little sodium sulphate the freezing point of water is lowered, but when the freezing occurs the ice which separates out is pure water, the sodium sulphate remaining in solution. If we dissolve more sodium sulphate the temperature at which ice precipitates is further lowered. The results thus obtained when plotted give us the curve *FCE*, which represents the lowering of the freezing point of water due to the presence of increasing amounts of sodium sulphate in solution, and represents all the conditions under which we can have solutions of sodium sulphate in contact with ice and in equilibrium.

Cryohydric Points. At *C*, a point corresponding to a temperature of $-1.2°$ and a concentration of 4 g., Na_2SO_4 per 100 g. water

in the solution, this freezing-point curve intersects the solubility curve of the decahydrate. At *E*, a point corresponding to a temperature of $-3.55°$ and a concentration of 14.5 g. Na_2SO_4 per 100 g. water in the solution, it intersects the solubility curve of the heptahydrate.

Let us start with a saturated solution in contact with solid decahydrate at some temperature above 0°, that is, somewhere on the curve *AC*, and let us cool the system. As we do so, more and more solid $Na_2SO_4.10\,H_2O$ forms and the solution becomes less concentrated. We thus travel downward describing the curve *AC* until we reach the point *C*. If here we did not strike the ice curve, there is no question but what more solid decahydrate would form and we should follow a route indicated by continuing the curve *AC*. But we do strike the ice curve, that is, we reach conditions for the precipitation of solid water, and ice must and does form. More solid decahydrate forms at the same time and, if we persist in trying to cool the system further, we do not succeed, but the solution solidifies as a whole to a mass of fine, intimately associated, but distinct crystals of ice and Glauber's salt.

Cryohydrates. This intimate mixture, this conglomerate, of distinct crystals thus formed is called a cryohydrate. Of course when the solidification is complete we may cool the solid mass as much as we please. If we turn about and starting with the solid cryohydrate raise the temperature gradually, when we reach $-1.2°$ the cryohydrate will begin to melt and the temperature will cease to rise until all the solid has melted. Thus cryohydrates have definite melting points, one of the characteristic properties of chemical compounds, but of course they are not chemical compounds, not only because they do not contain their constituents in their stoicheiometric proportions, but also because the individual crystals of the two substances are readily distinguished under a microscope.

The conditions and the phenomenon are exactly similar at the point *E*. As we descend the curve *DE* more and more of the solid heptahydrate forms as the temperature falls. When *E*, the temperature of $-3.55°$, is reached, crystalline water begins to precipitate also. Efforts to further cool do not lower the temperature but the solution solidifies as a whole to an intimate mixture of crystals of water and crystals of sodium heptahydrate. This too is a cryohydrate, though a metastable system. The Glauber's salt cryohydrate is evidently the stable system.

The points C and E at which cryohydrates form, and which give at once the percentage composition of cryohydrates and their characteristic melting points, are known as cryohydric points.

Continuity of Properties of the Solution as We Pass Transition Points. We may determine the numerical values of numerous properties of a saturated solution at a succession of different temperatures. In passing the point A there is no discontinuity in any of these properties, in the specific heat, in the coefficient of expansion, in the index of refraction, in any of the physical properties which we can measure. Therefore we are forced to the conclusion that we have always the same thing in solution whatever may be the particular hydrate which we have in the solid phase. It must be emphasized that these changes which we have been studying are always in the solid phase, not in the liquid phase. $Na_2SO_4.10\,H_2O$ is a distinct and different substance from $Na_2SO_4.7\,H_2O$ or from Na_2SO_4. If we clearly understand that these are three different substances it need cause no surprise that they have different solubilities and different solubility curves. What they have in common is the solution resulting from them. We are unable to detect any difference in solutions made from the three distinctly different solids. These facts are interesting to say the least, whatever interpretation may be put upon them.

From this discussion we see how careful we must be in speaking of the solubility of a substance to define exactly what substance we mean. It is not sufficient to say sodium sulphate, we must state also which hydrate it is to which the value refers.

Transition Points. Certain generalizations may be made which will apply not only to these, but to all similar cases.

Where solubility curves of two varieties intersect, the solubility of each variety is the same, and at this temperature there is always a change from one solid form to the other. It is a transition point.

Inclinations of the Curves. Two such solubility curves invariably make an angle with each other, but it is not necessary that the new form, appearing with increasing temperature, should show a diminishing solubility as the temperature rises. It, too, may be more soluble the higher the temperature, but the change in direction, the nick, or angle made by the intersection of the curves is always there, for it has been found that the variety formed at the higher temperature always shows a smaller increment of solubility with increasing temperature than the original variety. Thus succeeding

curves with ascending temperatures will have less and less inclination to the abscissa.

An Experimental Method of Reaching Metastable Regions. We can obtain metastable conditions experimentally as follows: Make a not-saturated solution of Glauber's salt without a particle of any solid present. Put this in a desiccator and hold the temperature constant. As the water evaporates the concentration increases and we are moving perpendicularly upwards on an ordinate corresponding to the temperature we choose.

An Experimental Method of Obtaining a Cryohydrate. Make a solution of Glauber's salt and cool it. In this way we are, as it were, traveling along some horizontal line in the diagram and nothing happens until we reach one of the solubility curves. What we shall get upon thus cooling depends upon the composition of the cryohydric mixture. If we have more salt present in our solution than corresponds to the cryohydric proportions, salt separates out first; if we have less, then solid solvent separates out first.

Whichever substance is in excess of the cryohydric proportions then separates out until, when the cryohydric temperature is reached, the solution has automatically taken on the cryohydric proportions, and at this temperature solidifies as a whole to the cryohydrate.

Application of Gibbs' Phase Law. We might from the outset have expressed all these facts regarding the solubility of sodium sulphate and its hydrates in the phraseology of the phase law. We have been studying the conditions of heterogeneous equilibrium in a system of two components, and the formulation $C + 2 - P = F$ applies. There being two components we have one degree of freedom when three phases are present, and these conditions are represented by the solubility curves AB, CA, ED, and also by FCE which represents equilibrium between solid ice, liquid solution, and the vapor phase.

Quadruple Points. In this figure the points determined by the intersections of curves are not triple points as they were in figures representing one-component systems; they are quadruple points, representing the conditions for the simultaneous existence of four phases in contact and in equilibrium. For instance, at A we have the four phases, the decahydrate, the anhydrous salt, the solution, and the vapor phase; at C we have the four phases, the decahydrate, solid water, the solution, and the vapor phase. D and E likewise are quadruple points, analogous to A and C but with the substitution of

the heptahydrate for the decahydrate. The formulation of the phase law teaches us that in systems of two components when four phases are present there is no degree of freedom; the system is invariant, represented by a point on the diagram.

Manifestly the systematic study of the solubility of a substance, with the assistance of the graphical method of representing results and of the phase rule as our guide in classification, brings out much that is interesting, and in a form in which the information is readily comprehended and retained.

Freezing Mixtures. We can form a clear conception of the way in which freezing mixtures act, and can foretell the optimum conditions from a knowledge of these solubility curves and cryohydric points. Let us consider the most used freezing mixture, ice and salt. In Fig. 60, AB is the solubility curve of NaCl. At A $(-0.15°)$* there is a transition point and the solid becomes the hydrate, $NaCl \cdot 2H_2O$. AC is the solubility curve of this hydrate and it ends in the cryohydric point C, at $-22.4°$, and corresponding to a concentration of the solution equal to 30 g. anhydrous NaCl per 100 g. H_2O.† FC is the freezing-point curve, ending also, of necessity, in the cryohydric point.

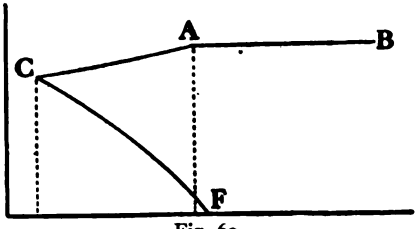


Fig. 60.

Mechanism of Freezing Mixtures. We mix salt and finely powdered ice or snow. If any liquid water is present salt dissolves in it. If we mix the solids below 0°, water vapor comes from the solid ice and this gas, not being in equilibrium with solid salt, condenses on the salt surface and we get salt solution. This concentrated salt solution is in contact with ice. The only conditions under which we can have this system in equilibrium are included in the curve FC.

Heat of Fusion of Ice the Source of Cooling. The curve shows that at 0° we can have no salt at all in solution, therefore some ice must melt to increase the dilution. In order to melt it must take up energy in the form of heat. If the system is insulated from the

* W. Meyerhoffer and A. P. Saunders, *Zeitschr. f. phys. Chem.*, **28**, 461 (1899).

† W. Meyerhoffer. Landolt, Börnstein, and Meyerhoffer, "Tabellen," third edition, p. 556.

surroundings it must get the heat at the expense of its own internal energy, therefore it cools itself off.

Three Possibilities. This additional water will dissolve more salt and the equilibrium is again upset, more ice is forced to melt, and the cooling goes further. This continues until one of three things happens. Either all the salt is dissolved and we reach equilibrium somewhere on curve *FC*, or all ice melts and we reach equilibrium somewhere on curve *AC*, or the cryohydric temperature and conditions are reached and no more cooling can occur for no more ice will melt. Thus we see the cryohydric temperature is very significant for a freezing mixture giving as it does the lowest temperature attainable under the most advantageous conditions with that combination.

Whether or not this lowest temperature for a given freezing mixture is actually obtained depends upon a variety of circumstances, largely upon how perfectly the system is insulated from the surroundings, and of course upon the quantity of the substances. The quantity of heat absorbed is determined by the heat of liquefaction of the ice melted. If this absorption is enough to reduce the temperature of the system from its initial temperature, whatever that may be, to the cryohydric point, in spite of losses by radiation and by simultaneous cooling of containing vessels, it will do so, otherwise not.

It is also clear that the most economical use of the substances is realized when they are mixed in the proportions of their cryohydrate. If the cryohydric temperature is reached and an excess of either substance remains, that excess is wasted.

Other Freezing Mixtures. The compositions and melting points of cryohydrates with most of the more commonly met salts, acids, and alkalies have been determined, and may be found in Landolt, Börnstein, and Meyerhoffer's "Tabellen." Not many, however, are actually utilized for freezing mixtures as cooling can be produced more conveniently and economically in other ways. The cryohydrate consisting of an intimate mixture of crystals of $CaCl_2 . 6 H_2O$ and ice which separates out from a solution containing 42.5 g. anhydrous $CaCl_2$ per 100 g. water, at $-55°$ has often been used. Several cryohydrates are known in the system of which SO_3 and H_2O may be considered as the two components, and a mixture of about equal weights of H_2SO_4 and ice is a convenient means of obtaining a temperature of about $-37°$.

Solubilities of Ferric Chloride Hydrates.* It is desirable to

* H. W. B. Roozeboom, *Zeitschr. f. phys. Chem.*, 10, 477–503 (1892).

consider one more set of solubility curves which bring out several interesting points not shown on the sodium sulphate diagram. Figure 61 contains the solubility curves of ferric chloride and of four hydrates of the same substance.

AB is a freezing-point curve giving the conditions for equilibrium between solutions of ferric chloride and ice. *B* is a cryohydric point (at $-55°$), the cryohydrate consisting of ice and ferric chloride

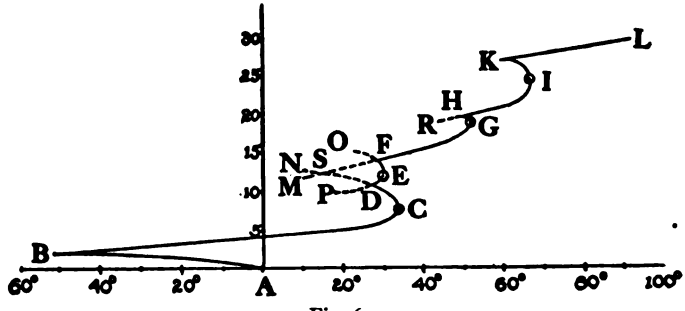


Fig. 61.

dodecahydrate ($Fe_2Cl_6 . 12 H_2O$). *BCD* is the solubility curve of the dodecahydrate. The curve turns at *C*, a temperature of 37°. At *C* the solution has the same percentage composition as the solid phase and at this point the whole solution will solidify at a constant temperature; in other words, this is the melting point of the dodecahydrate.

Two Saturated Solutions. Erect a perpendicular corresponding to 36° and it cuts the curve *BCD* twice. We have two solubilities, two saturated solutions in equilibrium with one and the same solid.

We may explain this rather peculiar phenomenon as follows: Consider the dodecahydrate, $Fe_2Cl_6 . 12 H_2O$ as a pure substance in which other substances may be dissolved. Its melting point, or freezing point, is 37°, indicated by point *C* on the diagram. If we add a foreign substance to any solvent whatsoever we lower its melting point. From *C* to *D* we have more Fe_2Cl_6 in the solution than corresponds to the dodecahydrate. This excess Fe_2Cl_6 may be considered as a foreign substance dissolved in a pure solvent and, of course, the freezing point of this pure solvent is lowered, as shown by the curve *CD*. Points on the curve below *C* toward *B* correspond to more water in the liquid phase than is in the dodecahydrate. We may consider water as the foreign substance dissolved in the pure solvent $Fe_2Cl_6 . 12 H_2O$ and the presence of this foreign substance, this water, lowers the freezing point of the solvent.

We have a precisely similar state of affairs at the points, *E*, *G*, and *I*, each of which corresponds to the melting point of a pure hydrate, *E* to the melting point of the heptahydrate, *G* to the melting point of the pentahydrate, *I* to the melting point of the tetrahydrate. In each instance the curve turns in such a way that at a temperature slightly below these melting points we have two solubilities. The above explanation applies to all of these curves.

Transition Points. At the point *D* (temperature 27.4°) a new hydrate with 7 H_2O appears in the solid phase. *D* is then a transition point. *DEF* is the solubility curve for this heptahydrate. At *F*, a second transition point, the pentahydrate appears in the solid phase, and *FGH* is its solubility curve. At *H*, a third transition point, the tetrahydrate appears and *HIK* is its solubility curve. At *K*, the fourth transition point, we have the anhydrous salt forming in the solid phase and *KL* is its solubility curve.

Cryohydric Points. At the cryohydric point *B* the whole system will solidify to a mechanical mixture of the dodecahydrate and ice. *D* is also a cryohydric point, where the whole system may solidify to a mechanical mixture of the heptahydrate and the dodecahydrate. A third cryohydric point at *F* corresponds to the conditions under which the whole may solidify to a mechanical mixture of the hepta- and pentahydrates. *H* is a fourth and refers to the penta- and tetrahydrates, and fifth and last, *K* is the cryohydric point for the tetrahydrate and anhydrous salt.

Metastable Cryohydrate. It is possible, by working carefully, to pass along the curve *CDN* and also along the curve *FM* until these two curves intersect at the point *S*. Those portions of the curves represented by dotted lines in the diagram correspond to metastable conditions. The point *S* is obviously a cryohydric point. It is a metastable cryohydrate which forms here as a mechanical mixture of the dodecahydrate and the pentahydrate.

Eutectic Mixtures. The melting point of bismuth is lowered by the presence of tin and the melting point of tin is lowered by the presence of bismuth. If we determine the melting points and plot them on the ordinate against percentage composition on the abscissa, as shown in Fig. 62, we see the two curves must cut each other. The intersection must correspond to a mixture with the lowest possible melting point. Guthrie* found the mixture containing 46.1 per cent Bi and 53.9 per cent Sn possessed such a minimum melting point

* *Phil. Mag.* (5), 17, 462 (1884).

at 133°. This mixture has a definite and constant melting point at this temperature as if it were a pure substance, but it is not. It is an intimate mixture, a conglomerate of fine crystals which may be distinguished by means of a microscope. Guthrie called this mixture with a minimum, constant melting point a eutectic mixture.

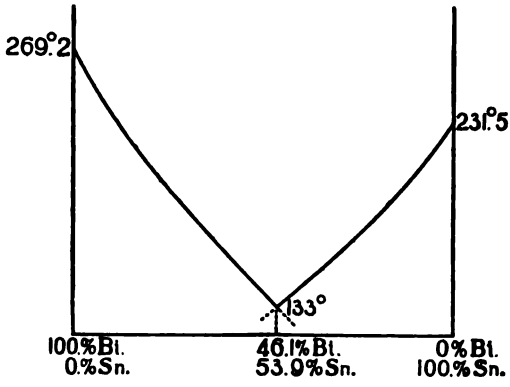


Fig. 62.

He found several others, for instance: 55.58 per cent Bi and 44.42 per cent Pb is a eutectic mixture melting at 122.7°; 59.19 per cent Bi and 40.81 per cent Cd is another melting at 144°.

He found he could still further lower the melting point by adding a third metal and a fourth. He prepared a eutectic mixture containing 47.45 per cent Bi, 19.39 per cent Pb, 13.31 per cent Cd, and 20 per cent Sn which melted at 71°.

Eutectic mixtures have since been determined for a great variety of other metals and salts and it would be interesting to deal with some of these in detail and indicate how we may have two or more eutectic mixtures with one pair of substances, etc., if space permitted.*

Eutectic mixtures are in principle the same as cryohydrates, indeed we may say cryohydrate is the name we give to a eutectic mixture when one of the components is water.

Distribution or Partition Coefficient. Bromine is slightly soluble in water and much more soluble in carbon disulphide, while water and carbon disulphide are practically insoluble in each other. Let C_1 be the concentration of a saturated solution of bromine in water and C_2 the concentration of a saturated solution of bromine in carbon disulphide. Now suppose we have both water and carbon disulphide in one vessel and add some bromine. We have found by experiment that the bromine will distribute itself between the two solvents in the ratio $\frac{C_1}{C_2}$; that is, the concentration of the bromine in the water

* See, for instance, Heycock and Neville, *Phil. Trans.* 189 A, pp. 25–69. 1897.

phase will be to the concentration of the bromine in the carbon disulphide phase as the solubilities of the bromine in these two phases. The distribution of a solute is found to take place in this way no matter what the particular actual concentrations may be. This has been proved to hold for a large number of instances and this ratio is called the distribution or partition coefficient. It varies with the temperature, of course, because the individual solubilities vary with the temperature.

This law holds only if the solute is in the same molecular condition in both solvents. If dissociation or association occurs in either solvent it does not. It could not be expected to hold, for upon dissociation or association we cease to have the original substance and have a new substance or new substances. For instance, the law does not hold for the distribution of benzoic acid between water and benzene. We have reason to believe that benzoic acid in benzene consists of "double molecules."

Extraction in One Step. We have here the underlying principle of the much used process of extraction.

Suppose our two solvents to be water and benzene, and that 100 g. of a substance twice as soluble in benzene as in water is dissolved in 1000 cm^3 of water. Shake this up with 1000 cm^3 of benzene. The solute will distribute itself between the solvents until its concentration in benzene is double its concentration in water. The benzene will then extract 66.6 g. of the substance and 33.3 g. will be left in the water. By this one shaking up we have thus extracted 66 per cent of the substance.

Extraction in Two Steps. Now suppose we have the same quantity of the same solution and shake it up with only 500 cm^3 of benzene. The proportions between the concentrations will be the same as before, of course. Then this 500 cm^3 of benzene will take out just half the substance from the water and leave half behind. Separate, and shake the remaining water solution with 500 cm^3 of fresh benzene and this second operation extracts half of what is present, as before. The total amount extracted from the water by these two shakings is thus 75 per cent of the original amount. We thus see that it is decidedly advantageous to use a given quantity of extracting material in successive small portions rather than all at once.

It will be recognized that the applications of these principles are numerous and important.

CHAPTER XXV

VELOCITIES OF CHEMICAL REACTIONS

Chemical Kinetics and Chemical Statics. The study of the mechanism of chemical reactions is often called chemical mechanics. It may be divided into two parts, chemical kinetics or dynamics, that is, the study of the rates or velocities of reactions, and chemical statics, or the study of conditions when the reactions have proceeded to the point where equilibrium is reached. We shall consider some of the fundamental facts and theories of the first topic in this chapter and of the second topic in the next.

A brief historical sketch of the development of the subject served as an introduction to Chapter VI and that occasion was taken to review the definitions of certain terms, doubtless familiar from previous courses. It may be as well to repeat that we owe the conception of the velocity of reaction to Wenzel (1777), and the conceptions of reversible reactions and equilibrium, as well as the first announcement of the law of mass action, to Berthollet (1801).

Heterogeneous and Homogeneous Systems. Chemical reactions may occur between different phases, when of course the seat of activity is the surface common to two phases. Such systems are called heterogeneous, and, as has been brought out, Gibbs' phase law is our most fundamental and useful generalization and guide in their study. Chemical reactions may also occur within one phase as, for instance, reactions between dissolved substances. Such a system is called homogeneous and Gibbs' phase law tells us nothing at all as to either occurrences or equilibrium conditions in homogeneous systems. In these cases the law of mass action is our most fundamental and useful generalization.

Law of Mass Action. As this law, in some of its applications at least, is familiar to all students before they reach this point in their studies, it is permissible to depart from our rule and state the generalization before examining the experimental facts in detail. The law of mass action as accepted to-day may be expressed as follows: Temperature being held constant, the velocity of a chemical reac-

tion is directly proportional to the product of the concentrations of the reacting substances.

Experimental Difficulty. Though entirely clear in his own mind regarding the above principles, Berthollet was unable to verify them experimentally, and this necessary step was taken by others much later. The problem is not an easy one, for it is necessary to determine the concentrations of reacting substances while they are reacting, to obtain, as it were, instantaneous photographs of continuously altering concentrations.

Inversion of Sugar. The first solution we owe to the ingenuity of L. Wilhelmy (1812–1864), who, in 1850, published his experimental investigation upon the rate at which cane sugar, in water solution, is converted to dextrose and lævulose by the catalytic action of acids according to the reaction, $C_{12}H_{22}O_{11} + H_2O = 2\,C_6H_{12}O_6$.*

Cane sugar rotates the plane of polarized light to the right; the mixture of dextrose and lævulose rotates it to the left. Wilhelmy caused this reaction to proceed in a polariscope holding the temperature constant, and observed the progress of the reaction in terms of degrees through which the plane of polarized light was rotated after the lapse of definite time intervals.

Formulation. If dx represents the small amount of cane sugar which disappears in the small time interval dt, the velocity of the reaction is $\frac{dx}{dt}$. Wilhelmy recognized that the amount reacting per unit time is proportional to the amount present (concentration) at that time; in other words, he knew and used the law of mass action. If A represents the amount of cane sugar present at the outset and x represents the amount which has disappeared after the lapse of time t, then $A - x$ represents the concentration at the end of time t, and the velocity $\frac{dx}{dt}$ is proportional to $A - x$.

The Velocity Constant. The velocity is proportional to, not equal to, the concentration. In order to use the equality sign we must introduce a proportionality factor, k, called the velocity constant, and then we may write, $\frac{dx}{dt} = k\,(A - x)$.

Integration of this equation gives, $-\,ln\,(A - x) = kt +$ constant. The integration constant may be eliminated as follows: When no

* *Pogg. Annal.*, 81, 413–433, 499–526 (1850). Also reprinted in Ostwald's "Klassiker der exakten Wissenschaften," No. 29.

time has elapsed, $t = 0$, and no substance has reacted, so $x = 0$. Substituting we have $-lnA$ = constant, therefore

$$-ln(A-x) = kt - lnA \text{ or } kt = lnA - ln(A-x), \text{ or } k = \frac{1}{t} ln \frac{A}{A-x}.$$

Briggs' logarithms multiplied by 2.3025 give natural logarithms, therefore we may write, $k = \frac{1}{t} 2.3025 \log \frac{A}{A-x}$. This constant factor 2.3025 may be included in k and we may write, $k = \frac{1}{t} \log \frac{A}{A-x}$.

We are not as a rule particularly interested in the actual numerical value of k, but we are very much interested in its constancy or lack of constancy. If it is constant, when the values for t, A, and x are varied through a wide range, it is strong evidence that the reasoning by which we reached the formula is correct.

In one of his experiments Wilhelmy found 46.75° right rotation at the beginning, and after waiting until the inversion was practically complete found 18.70° left rotation. The total change, measured in terms of angle of rotation was then 46.75° + 18.70° or 65.45°, and as this rotation is directly proportional to the amount of cane sugar present, it may be used as well as grams or any other unit as a measure of the concentration of the sugar, and may be inserted in the equation as the value A. The change in the angle is a measure of the sugar inverted. For instance, at the expiration of 45 minutes he observed a rotation of 38.25°, and so 46.75° − 38.25° = 8.5° is the measure of the change or x. Substituting in the formula we have:

$$k = \frac{1}{45} \log \frac{65.45}{65.45 - 8.5} = 0.001\,344.$$

The following table gives actual experimental values obtained by Wilhelmy and the corresponding velocity constants.*

t in minutes.	Angle rotation.	$k = \frac{1}{t} \log \frac{A}{A-x}$.
0	46.75	.....
45	38.25	0.001344
90	30.75	0.001352
150	22.00	0.001321
210	15.00	0.001371
270	8.25	0.001425
390	−1.75	0.001499
510	−7.00	0.001463
630	−10.80	0.001386
	−18.70	

* The values in this table were taken from Ostwald, "Lehrbuch der Allgemeinen Chemie," Vol. II (2), p. 202.

Though the values of t, A, and x vary greatly, the values for k are in fact nearly constant, and so our reasoning is, in all probability, correct.

Reactions of the First Order. This formulation applies wherever the concentration of only one substance alters in the course of the reaction. All " one-substance " reactions are called reactions of the first order, or unimolecular (sometimes monomolecular) reactions. It is true that in our example two substances interacted, cane sugar and water, but the quantity of water disappearing was negligible as compared to the large amount present, for the experiment was carried out in water solution. The concentration of the water was practically constant and that of the sugar was the only concentration changing.

Though Wenzel, Berthollet, and Wilhelmy surely knew the law of mass action and Wilhelmy developed the formula we have just been considering, C. M. Guldberg and P. Waage first systematized the subject and made clear the universality of the law, in 1864.*

We cannot spare the time to follow the somewhat involved historical sequence of ideas and experiments but shall proceed according to the methodical classification now in use.

Other Unimolecular Reactions. Many other reactions have been measured and have been found to run according to the formulation developed by Wilhelmy for the inversion of sugar. For instance, the action of light on a solution of chlorine in water giving hydrochloric acid and free oxygen, the reduction of potassium permanganate by a large excess of oxalic acid, the reduction of hydrogen peroxide according to the reaction $H_2O_2 + 2\,HI = 2\,H_2O + 2\,I$, the saponification of methyl acetate according to the reaction $C_2H_3O_2CH_3 + H_2O = CH_3OH + C_2H_3O_2H$, the conversion of dibromsuccinic acid into bromfumaric acid and hydrobromic acid, which occurs according to the reaction $C_4H_4O_4Br_2 = C_4H_3O_4Br + HBr$ upon boiling a water solution, have all been shown to run according to that formulation, and are therefore to be called reactions of the first order, or unimolecular.

The Progress of Unimolecular Reactions. The formula being logarithmic we see that theoretically at least the reaction will never

* A paper in Norwegian, presented at Christiania in 1864. "Études sur les affinités chimiques" (1867), and *Jour. prakt. Chem.* (2), **19**, 69–114 (1879). These papers are all reprinted in Ostwald's "Klassiker der exakten Wissenschaften," No. 104. Another book which had much influence upon the development of the subject is "Études de dynamique chimique," by J. H. van't Hoff (1884).

reach an end, but will approach a limit slower and slower. But for all practical purposes we may consider it at an end when 0.999 of the original amount has disappeared, and we can calculate the time needed for this very easily.

The equation $k = \frac{1}{t} ln \frac{A}{A-x}$ is the same as $0.4343\ kt = \log \frac{A}{A-x}$. When half of the original amount has disappeared $x = \frac{A}{2}$. Substitute this value and we have, $0.4343\ kt = \log 2 = 0.3010$. When 0.999 of the original amount has disappeared $x = 0.999\ A$. Substitute this value and we have, $0.4343\ kt = \log 1000 = 3$. Thus the time required for 0.999 of any original quantity to react is ten times the time required for half to react.

Notice also that the numerical value of k is the same whatever the units we employ to measure quantities. $\frac{A}{A-x}$ is a ratio and so $\log \frac{A}{A-x}$ has the same value if we express A and x in grams or milligrams, in molecular weights, degrees and minutes of rotation of the plane of polarized light, or in any other units whatever.

Theory. We do not know what causes a chemical reaction to occur, but applying our molecular theory we may imagine conditions something as follows: Suppose we have a unimolecular reaction and 1000 molecules present to begin with. Suppose one molecule in ten reacts in one minute. Then 100 will react during the first minute and 900 will be left. Ninety will react during the second minute, leaving 810. Eighty-one will react during the third minute, and so on. The number reacting is directly proportional to the number present. This is merely a special and simple illustration of the law of mass action. If C_1 represents the concentration at any time, we may write, $\frac{dx}{dt} = kC_1$ and this is the same as the formulation we have been using, for C_1 is the same as $A - x$.

Reactions of the Second Order. Now suppose the reaction is between two substances and that the concentration of each diminishes appreciably. A molecule of the first substance must come in contact with a molecule of the second before they react. We cannot say that at each contact reaction occurs; there may be a vast number of contacts and only one out of a hundred, or one out of a thousand, may be of just the right character to result in a reaction. However the

mechanism may be imagined, it is evident that doubling the concentration of the first substance, while the concentration of the second remains the same, doubles the contacts per unit time, and doubles the juxtapositions suitable for the reaction to occur, that is, it must double the velocity of the reaction. On the other hand, doubling the concentration of the second substance while the concentration of the first remains the same must double the velocity. If we double both concentrations we must then have four times as many suitable contacts per unit time. If we treble both concentrations we must have nine times as many contacts per unit time. These are very simple applications of the theory of chances, and they show that the velocity of the reaction must vary as the *product* of the concentrations of the reacting substances.

Formulation. If we represent the concentrations by C_1 and C_2 we may formulate the velocity of a reaction of the second order, or bimolecular reaction, as $\frac{dx}{dt} = k C_1 C_2$, where k is the velocity constant.

Let A and B represent the quantities of the two interacting substances originally present, expressed in chemical units, in gram-molecular weights. Let x represent the number of gram-molecular weights of one substance which has gone into reaction after the lapse of time t. x must then also express the number of gram-molecular weights of the second substance which has entered into the reaction and also the number of gram-molecular weights of the products formed. Then the velocity of the reaction at the time t is expressed in the equation, $\frac{dx}{dt} = k (A - x) (B - x)$.

We have the simplest case when we start with equimolecular quantities. Then $A = B$ and the equation becomes $\frac{dx}{dt} = k (A - x)^2$ or $dt = \frac{1}{k} \frac{dx}{(A - x)^2}$. Integrating we get $t = \frac{1}{k} \frac{1}{A - x} +$ constant. When $t = 0$, $x = 0$, and so the integration constant $= -\frac{1}{kA}$. Substituting this value and simplifying we get, $k = \frac{1}{t} \frac{x}{A (A - x)}$.

Experimental Verification. A number of early investigators found experimental values demonstrating, more or less satisfactorily, the applicability of this formulation. But the first example quite free from objections was furnished by R. B. Warder.* He saponified

* *Am. Chem. Jour.*, 3, 340–351 (1882). Ostwald, "Lehrbuch," Vol. II (2), p. 215.

ethyl acetate in water solution with an equivalent quantity of sodium hydroxide. At the expiration of measured times he ran a definite volume of his reacting solution into an excess of acid and titrated back, thus determining the concentration of the sodium hydroxide left at those times. He obtained the following values:

t in minutes.	x	Ak
5	5.76	0.113
15	9.87	0.107
25	11.68	0.108
35	12.59	0.106
55	13.69	0.108
120	14.90	0.113

The value Ak is satisfactorily constant and as A, the original amount, is of course constant, this proves that k is constant and thus we have experimental evidence that shows our reasoning regarding bimolecular reactions is probably correct.

We may write this reaction:

$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH,$$

or, in the light of the dissociation theory as,

$$CH_3COOC_2H_5 + Na^{\cdot} + OH' = CH_3COO' + Na^{\cdot} + C_2H_5OH.$$

In this latter form it might appear as though three substances entered into the reaction, but it will be observed that the concentration of the sodium ion remains constant throughout. It may then be omitted and we may rewrite this second form as,

$$CH_3COOC_2H_5 + OH' = CH_3COO' + C_2H_5OH,$$

and it becomes apparent that the only concentrations which alter are those of the ester and the hydroxide ion. In other words this is a typical reaction of the second order.

Other Bimolecular Reactions. Among other reactions which have been studied and proved to follow the formulation for reactions of the second order are: the action of acids on acetamide* and the action of sodium hydroxide on sodium monochloracetate.† If A' represents the acid radical anion we may write the first reaction,

$$CH_3CONH_2 + A' + H^{\cdot} + H_2O \rightleftharpoons NH_4^{\cdot} + A' + CH_3CO_2H.$$

* Ostwald, *Jour. f. prakt. Chem.*, **27**, 1–39 (1883), and "Lehrbuch," Vol. II, (2), p. 215.

† van't Hoff, "Études de Dynamique Chimique," p. 20, and Ostwald, "Lehrbuch," Vol. II, (2), p. 215.

The reaction is carried out in water solution and so the concentration of the water does not alter appreciably. The concentration of the acid anion clearly remains unaltered and the only concentrations which alter are those of the acetamide and the hydrogen cation. It is then a bimolecular reaction and the experimental results inserted in the formula give a constant value for k.

We write the second reaction, in the light of the dissociation theory,

$$CH_2ClCOO' + Na^{\cdot} + Na^{\cdot} + OH' = CH_2OHCOO' + Na^{\cdot} + Na^{\cdot} + Cl'.$$

The concentration of the sodium ions remains constant. The concentrations of only two substances vary, and this too is a bimolecular reaction. The experimental results give satisfactorily constant values for k.

General Characteristic of Second-order Reactions. Attention was called to the fact that with reactions of the first order the numerical value of the velocity constant k is the same, no matter in what units we express the concentrations. This is not true for reactions of the second order. Suppose we adopt a given unit and insert in the formula $k = \frac{1}{t}\frac{x}{A(A-x)}$ and then adopt a unit one-half as large. The values become $k = \frac{1}{t}\frac{2x}{2A(2A-2x)}$, or $k = \frac{1}{t}\frac{x}{2A(A-x)}$ and obviously the numerical value of k is one-half what it was.

Again, it was shown that with a monomolecular reaction the time required for a given fraction, say one-half, of any original amount to enter into reaction was always the same no matter what the original amount might be. This is not true for bimolecular reactions. Consider the condition when half has reacted. Then $x = \frac{A}{2}$. Substituting in the formula, we have,

$$k = \frac{1}{t}\frac{\frac{A}{2}}{A\left(A - \frac{A}{2}\right)} \quad \text{or} \quad k = \frac{1}{tA} \quad \text{or} \quad t = \frac{1}{kA}.$$

In words, the time required for a given fraction to enter into reaction is inversely proportional to the original amount. Double the original concentrations and the reaction will be half over in half the time.

When Original Amounts Are not Equivalent. In case the two substances are not present in equivalent quantities we must integrate the expression $\frac{dx}{dt} = k(A-x)(B-x)$ as it stands. This gives a

much more complicated formula which will be omitted. Suffice it to say that experimental verification of the formula has been obtained.

Reactions of the Third Order. If, according to the equation, three different molecules must meet in order that the reaction shall occur, the same reasoning gives the formula $\frac{dx}{dt} = kC_1C_2C_3$ where C_1, C_2, and C_3 are the three concentrations which vary in the course of the reaction.

Formulation. If A, B, and C are the original quantities and x the amount of each expressed in chemical units, which has entered into reaction at the time t, then $\frac{dx}{dt} = k(A-x)(B-x)(C-x)$. The simplest case is when we begin with equivalent quantities. Then the equation becomes $\frac{dx}{dt} = k(A-x)^3$. Integrating and eliminating the integration constant we obtain, $k = \frac{1}{t}\frac{x(2A-x)}{2A^2(A-x)^2}$.

The first reaction proved experimentally to follow this formulation is that between ferric chloride and stannous chloride.* We may write this reaction, $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$ or, better, in the light of the dissociation theory, $2Fe''' + Sn'' = 2Fe'' + Sn''''$. Two ferric ions and one stannous ion must meet in some particular way for the change to occur. Thus we see that for a reaction to be of the third order it is not necessary that the three molecules should be different.

The following table gives a few of the experimental values. The velocity constant as calculated by the formula is given under k_3. The velocity constant calculated by the formula for a reaction of the second order is given under k_2. k_3 is satisfactorily constant while k_2 is not.

t	x	$A-x$	k_2	k_3
1	0.01434	0.04816	4.8	88
3	0.02586	0.03664	3.8	81
7	0.03612	0.02638	3.1	84
11	0.04102	0.02148	2.8	87
17	0.04502	0.01748	2.4	89
25	0.04792	0.01458	2.1	89
40	0.05058	0.01192	1.7	85

* A. A. Noyes, *Zeitschr. f. phys. Chem.*, **16**, 546–561 (1895).

Other Reactions of the Third Order. The reaction between potassium chlorate and ferrous chloride in acid solution, and between silver acetate and sodium formiate, have been shown to conform to the formulation for the third order.

In General Regarding Third-order Reactions. Let us consider what we shall have when a reaction of the third order has run until half the original quantities have disappeared. Then $x = \frac{A}{2}$. Substituting this in the formula and simplifying we get, $k = \frac{1}{t}\frac{3}{2A^2}$. This shows us that as with reactions of the second order, the numerical value of k is dependent on the units we use to express our quantities.

If we rewrite the equation as follows: $t = \frac{1}{k}\frac{3}{2A^2}$ we see that the time required to reach the stage of half completion is inversely proportional to the square of the original amount.

Determining the Order of a Reaction. Of course the first step in determining the order of a reaction is to calculate the constants according to the formulations for the different orders. Generally only one set of " constants " shows any degree of constancy, the others showing a fairly regular increase or decrease. If the most constant set of values for k is obtained with the formulation for the third order the reaction is probably of that order.

Owing to the experimental difficulties involved in catching and determining conditions, on the fly as it were, sometimes no set of values for k shows the wished for constancy. Moreover, the progress of one reaction is often partly concealed by the occurrence of simultaneous side, or secondary, reactions. We can sometimes determine the order of the reaction even under decidedly adverse conditions of this character by altering the initial concentrations and determining the time required to reach a given stage.

We saw that if the reaction is of the first order the time required to reach a given stage is not altered by altering the original concentration. Suppose one-half of some original amount is found to disappear in 10 minutes. Repeat, using double the concentration. One-half of this larger amount will disappear in 10 minutes.

We saw that if the reaction is of the second order the time required to reach a given stage is inversely proportional to the original concentration. Suppose one-half of some original amount is found to

disappear in 10 minutes. Repeat, using double the concentration. One-half of this larger amount will disappear in 5 minutes.

We saw that if the reaction is of the third order the time required to reach a given stage is inversely proportional to the square of the original concentration. Suppose one-half of some original amount is found to disappear in 10 minutes. Repeat, using double the concentration. One-half of this larger amount will disappear in 2.5 minutes. The application of this simple reasoning to other alterations of concentrations, which may be experimentally more convenient, is sufficiently obvious. This is a powerful instrument for determining the order of a reaction even though the sets of constants are decidedly irregular.

Reactions of Higher Orders. If four molecules have to meet, and four concentrations vary, we have a quadrimolecular reaction, or reaction of the fourth order. Integration leads to formulæ of greater and greater complexity and they will be omitted. The reaction between bromic and hydrobromic acids giving bromous and hypobromous acids has been shown to correspond with the formulation for a fourth-order reaction.* We may write the reaction:

$$2\,H' + Br' + BrO_3' = HBrO + HBrO_2.$$

If five molecules must meet, and five concentrations vary, we call the reaction quinquimolecular, or of the fifth order. The reaction

$$2\,KI + 2\,K_3Fe(CN)_6 = 2\,K_4Fe(CN)_6 + I_2$$

has been shown to run according to the fifth-order formulation.† To make clearer how this may be we write the reaction in the light of the dissociation theory,

$$2\,Fe(CN)_6''' + 3\,I' = 2\,Fe(CN)_6'''' + I_3'.$$

General Formulation. We may sum up the subject in one formula. All equations are included in the general form,

$$mA + nB + pC \ldots = qD + rE + sF \ldots$$

If C_1, C_2, and C_3 . . . represent the concentrations of the substance whose concentrations vary we have, $\frac{dx}{dt} = kC_1^m C_2^n C_3^p \ldots$

According to our molecular theory and the law of mass action the

* Judson and Walker, *Jour. Chem. Soc.*, 73, 410–422 (1898).

† Donnan and Rossignol, *Trans. Chem. Soc.*, 83, 703 (1903).

order of a reaction should be given by the sum of the exponents in this general formulation.

Most Reactions of Low Order. As a matter of fact reactions for which we must write more or less complicated equations are found to run according to the formulations for reactions of much lower order. For instance, if we apply the general formulation just given to the following reaction:

$$6\,FeSO_4 + KClO_3 + 3\,H_2SO_4 = 3\,Fe_2(SO_4)_3 + KCl + 3\,H_2O,$$

we shall have, $\frac{dx}{dt} = kC_1^6C_2C_3^3$ and the sum of the exponents is 10, or the reaction is of the tenth order. As a matter of fact it has been demonstrated by A. A. Noyes to run according to the formulation for a third-order reaction. Rewriting the equation in the light of the dissociation theory merely increases our difficulties, for we have,

$$6\,Fe^{\cdot\cdot} + ClO_3' + 6\,H^{\cdot} = 6\,Fe^{\cdot\cdot\cdot} + Cl' + 3\,H_2O$$

and then should write $\frac{dx}{dt} = kC_1^6C_2C_3^6$. The sum of the exponents is 13, or it is a reaction of the thirteenth order.

Almost all reactions run according to the first or second order, a very few according to the third, and one or two only according to the fourth and fifth. No reaction has yet been found running according to a higher order than the fifth.

Complex Reactions Probably Sequences of Simpler Reactions. Nernst has offered a plausible explanation for these discrepancies. As the number of molecules which must meet in one point before a given reaction can occur increases, the chances for such juxtapositions become rapidly less. The chances that three molecules shall meet in a point are very much fewer than that two shall so meet. The chances that four shall meet in a point are yet fewer. Consequently any reaction of an order higher than the second or third must be very slow indeed.

When, according to the equation, the reaction is of some high order, it doubtless occurs in steps. It reaches the end by a series of unimolecular or bimolecular reactions and so of course the experimental results fit these simpler formulations.

O. Knoblauch* has investigated an instance of this sort. Let us represent the radical of a dibasic acid by R''. Then the reaction rep-

* *Zeitschr. f. phys. Chem.*, **26**, 96–108 (1898).

resenting the saponification of its ethyl ester by sodium hydroxide is the following:

$$R''(C_2H_5)_2 + 2\,NaOH = R''Na_2 + 2\,C_2H_5OH.$$

Experimental results show that this is certainly not a trimolecular reaction. It may be imagined as running in two steps, first,

$$R''(C_2H_5)_2 + NaOH = R''(C_2H_5)Na + C_2H_5OH$$

and then $R''(C_2H_5)Na + NaOH = R''Na_2 + C_2H_5OH$. It amounts then to two bimolecular reactions occurring one after the other, and the experimental results correspond with the formulation derived on this basis.

Heterogeneous Systems and the Law of Mass Action. The law of mass action applies also to heterogeneous systems, systems in which the reacting substances are in different phases. The quantity which reacts in unit time is obviously and necessarily directly proportional to the area of the surface of contact.

In heterogeneous systems the products of the reaction are apt to separate the reacting substances and stop the reaction. Its continuation depends then largely upon the rate at which the products are removed. The velocity of a reaction between a solid and a liquid or a gas depends then in great measure upon the rate of diffusion.

Influence of Temperature on Velocity of Reaction. At room temperature the oxidation of carbon or the interaction of hydrogen and oxygen proceeds so slowly we cannot measure the velocity. On the other hand, the ordinary reactions of qualitative analysis, which we have reason to suppose occur between ions in water solution, occur so rapidly we cannot even estimate their velocity. The range then is enormous, from almost zero up to a value not even estimated. Most organic reactions are slow as, for instance, the growth of animals and vegetables. But this is by no means an invariable rule for our most violent explosives are organic compounds and an explosion is merely an exceedingly rapid reaction.

Van't Hoff observed that the velocity of a reaction is, as a rule, about doubled or trebled when the temperature is increased 10°. There are some reactions whose velocities are not increased quite so much, and others whose velocities are rather more than trebled by this increase of 10°. But we may say the temperature coefficient is of this order of magnitude for almost all reactions which have been measured.

This means that the velocity increases in geometric progression while the temperature increases in arithmetic progression. The result is rather surprising when first considered. Suppose a given reaction has a velocity of one at 0°. Assume a doubling for 10°, then the velocity will be two at 10°, 4 at 20°, 8 at 30°, 1028 at 100°, and 1 052 672 at 200°. We do not ordinarily realize how vastly we can hasten a reaction by comparatively small elevations of the temperature.

Why the velocity should increase so rapidly with the temperature is one of the most interesting of unanswered questions. According to the kinetic molecular theory, the square of the velocity of gaseous molecules varies directly as the absolute temperature. Thus an inincrease of 10°, from 273 to 283 absolute, will increase their velocity a little less than 2 per cent and this is wholly inadequate to account for the increased velocity of reaction.

Kindling Temperature. If a reaction can take place at all, it is, theoretically at least, occurring at any temperature, though often immeasurably slowly. If a lump of coal is heated the oxidation proceeds more rapidly. The reaction evolves heat and this is conducted away at such a rate that there is no increase in the temperature at the seat of reaction. But there is a temperature, different for different substances and for one substance different in different surroundings, at which the heat of the reaction is evolved faster than it is conducted away. Then the substance grows hotter, the reaction goes faster and this in turn heats things faster until we have incandescence, flames, and the accompanying phenomena of combustion. The lowest temperature at which this self-intensification sets in may be called the kindling temperature. The kindling temperature is thus not a fixed point even for one substance and depends upon a number of factors.

Spontaneous Combustion. Animal or vegetable oil in a pile of cotton waste oxidizes. The cotton is a poor conductor of heat and so the spot grows warmer. The reaction goes faster and the heating may result in "setting fire" to the whole, and we have so-called "spontaneous combustion," the source of many fires. Spontaneous combustion used to occur frequently in cargoes of baled cotton. Mineral oils, which have now superseded others for use about machinery, do not oxidize in the air and so are less dangerous.

Catalysis. When a substance by its mere presence alters the velocity of a reaction, and may be recovered unaltered in nature or

amount at the end, it is called a catalytic agent or catalyzer, and the phenomenon is called catalysis.*

Instances. Every student becomes familiar with a number of examples of catalytic action in his first course in chemistry. He learns that oxygen is evolved but slowly from potassium chlorate at relatively high temperatures and that the presence of manganese dioxide, which may be recovered unaltered in nature and amount, much hastens the reaction, that the presence of finely divided solids causes hydrogen peroxide to decompose rapidly, and so on. The lead chamber process for the manufacture of sulphuric acid is historically and technically an important instance of catalysis. The oxidation of sulphur dioxide to sulphur trioxide occurs but slowly. In the presence of oxides of nitrogen the velocity of the reaction is greatly increased. As early as 1806 Clement and Desormes demonstrated the formation of nitrosyl sulphuric acid and attributed the influence of these oxides to the formation and decomposition of this intermediate product. That the contact process for the manufacture of sulphuric acid, which has attained such importance in recent years, was strictly analogous, the finely divided platinum or iron oxide being the catalytic agent, was clearly brought out by Liebig.†

Influence of Solvent. Instances of catalysis may be multiplied almost without number. A given reaction occurs at different rates in different solvents. The solvent remains unaltered at the end of the reaction and hence all these effects must be reckoned with catalytic actions.

* In 1834 Mitscherlich concluded that the formation of ethyl ether and water from ethyl alcohol in the presence of sulphuric acid did not depend upon the dehydrating power of the acid nor upon the formation of an intermediate product, ethyl sulphuric acid, but that the sulphuric acid facilitated the reaction, by its mere presence, without entering into it. He called this contact action, a term in every way as appropriate as catalysis. The name catalysis was suggested by Berzelius in 1835.

† The importance of the phenomenon can hardly be overestimated and the practical value of numerous technical processes depends upon the use of catalytic agents. The following brief list will make this evident: The manufacture of glucose from starch by hydrolysis in which dilute acids act as catalytic agents; the oxidation of naphthalene to phthalic acid under the catalytic influence of mercury in the manufacture of indigo; Deacon's process in which copper chloride hastens the combination of hydrogen and chlorine to hydrochloric acid; the manufacture of aniline black with the assistance of vanadium; Friedel and Crafts' reactions with aluminium trichloride; condensation reactions which occur in the presence of chloride of zinc; reductions which occur in contact with nickel; Sandmeyer-Gatterman reactions, etc.

N. Menschutkin* measured the velocity of the reaction,

$$N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I$$

in a variety of solvents. In hexane the velocity constant, k, had the value 0.000 180; in heptane, 0.000 235; in benzene, 0.005 84; in ethyl alcohol, 0.0433; in benzyl alcohol, 0.133, and intermediate values in other solvents. The velocity is nearly one thousand times as great in benzyl alcohol as in hexane.

Extent of Catalytic Effect. The difference in velocity of the above reaction in hexane and in heptane is but slight, though the quantity of the catalytic agent is large, it being the solvent. The most fascinating instances of catalysis are those in which small traces of the catalyzer produce great effects, and we are rather too apt to assume that these alone are instances of catalysis. Some of the quantitative measurements are indeed striking. For instance, Bredig,† studying the increased velocity with which hydrogen peroxide decomposes in the presence of colloidal platinum, was able to detect such increase when the concentration of the platinum was but one seventy-millionth of a symbol weight per liter. Again, A. Titoff ‡ found that the velocity with which sodium sulphite was oxidized was increased 30 per cent by the presence of one-thousandth of a formula weight in grams of copper sulphate per liter.

Concentration of Catalyzer. The inversion of sugar occurs exceedingly slowly by itself, but is much hastened by the presence of any acid. The acid acts catalytically. If we begin with a very dilute strong acid § and then double its concentration we shall double the rate of the inversion. All acids in equivalent concentrations do not act alike, but those which produce the greatest effect give us the series of properties which cause us to conclude they are most completely dissociated into their ions. By carrying out experiments with a long series of acids, Ostwald was enabled to say the catalytic effect is directly proportional to the concentration of the hydrogen ion and has nothing to do with the anion except in rare instances. By the same line of reasoning it seems plausible to attribute many of the catalytic effects of bases to the hydroxyl ion and we find the effect proportional to the concentration of this ion. We shall revert to this topic in Chapter XXVI. It appears to be a fairly general rule that

* *Zeitschr. f. phys. Chem.*, **6**, 41–57 (1890).

† *Zeitschr. f. phys. Chem.*, **31**, 258–353 (1899).

‡ *Zeitschr. f. phys. Chem.*, **45**, 641–683 (1903).

§ For definition of "strong acid," see Chapter XXVI.

the catalytic effect is proportional to the concentration of the catalytic agent.

Water as a Catalyzer. Strictly dry silver chloride is hardly sensitive to light; strictly dry carbon monoxide will not burn in dry oxygen. Many similar instances may be cited to demonstrate that water frequently acts catalytically.

Autocatalysis. It sometimes happens that one of the products of a reaction acts catalytically on the reaction. This is usually the case when a metal dissolves in an acid. Put copper in pure nitric acid and the action is slow. One of the products is nitrous acid and this, acting catalytically, much increases the velocity. Thus this reaction increases in velocity as it proceeds. Ordinarily a reaction has its greatest velocity at the beginning. The characteristic course of a reaction involving autocatalysis is a velocity small at first, ascending to a maximum and then descending. Ostwald calls attention to the fact that this is also the characteristic course of fevers and it is highly probable that the resemblance is due to causes the same in principle.

Enzymes. Plants and animals produce ferments, substances similar to albumen and of unknown constitution which, in small quantities greatly hasten certain reactions. These are called enzymes. Before digestion can proceed, starch must be changed to sugar according to the reaction $(C_6H_{10}O_5)_n + n\,H_2O = n\,C_6H_{12}O_6$. The velocity of this reaction is much increased by the presence of traces of an enzyme called ptyalin, which occurs in the saliva, and other enzymes found in the pancreatic juice. Pepsin and trypsin are other enzymes which greatly hasten the digestion of albumen.

Enzymes are as a rule specific, each one capable of exerting its extraordinary effect on just one reaction. Another characteristic is their sensitiveness to the presence of other substances. They are easily "poisoned." If there were any doubt as to whether these interesting and important substances should be included among catalytic agents this doubt was removed by Bredig who demonstrated that the catalytic power of his colloidal metals was of precisely this character. They are readily "poisoned," and poisoned by the same substances which "poison" enzymes (by HCN, $HgCl_2$, and H_2S). The platinum used in the contact process for making sulphuric acid is likewise easily poisoned and rendered entirely useless as a catalytic agent by arsenic. Hence one of the most important parts of the contact process is the freeing of the gases from all arsenic.

Negative Catalysis. A number of instances are known of reactions which are retarded by the presence of small traces of other substances. For example, the writer was able to observe a distinct retardation of the rate at which sodium sulphite was oxidized by the air when the solution contained one one-hundred-and-sixty-thousandth of a formula weight of mannite per liter. The reaction was retarded also by exceedingly small quantities of benzyl alcohol, benzaldehyde, glycerol, phenol, and other substances.*

Explanations of Catalytic Effects. It is evident from their great variety, that one and the same explanation cannot be equally satisfactory for all instances of catalysis. Where we have been able to detect an intermediate compound with the catalyzer, such as nitrosyl sulphuric acid, we may formulate the mechanism as follows: The reaction $A + B = AB$ goes slowly, but the reactions $A + K = AK$ and $AK + B = AB + K$ go rapidly, and so the presence of K greatly facilitates the formation of AB. The really interesting question here is, why does $A + B = AB$ go slowly and why do $A + K = AK$ and $AK + B = AB + K$ go rapidly? For this question we have no answer. Our " explanation " is indeed but partial. Moreover, in the majority of interesting cases of catalysis the quantity of catalyzer is so small it is, to say the least, a severe strain to even imagine intermediate products.

When metals or other surfaces exert catalytic effects on reactions between gases we may plausibly assume that the gases are condensed on the surfaces and so brought in more intimate contact with each other and in greater concentrations. It is entirely probable that colloidal metals attract and condense dissolved substances on their surfaces (adsorption) and so facilitate reactions in solutions. How far this explanation may be extended to apply to other catalytic agents in solutions is not certain.

Though these explanations may be considered as fairly satisfying as far as they go, yet there are many cases of catalysis without experimental evidence justifying us in applying them. For example, we have no experimental ground for assuming the existence of an intermediate compound in perhaps the most familiar instance of catalysis, the effect of manganese dioxide on the decomposition of potassium chlorate.

While thus we have no adequate generally applicable explanation of catalysis we should not think of the phenomenon as peculiarly

* *Zeitschr. f. phys. Chem.*, 26, 493–532 (1898).

mystifying. Let us rather remember that we have no adequate explanation of the fact that chemical reactions occur at all. When we have obtained this we may be in a better position to understand why one occurs slowly, another rapidly, and why other substances influence these velocities. Until then we must content ourselves as usual with describing and formulating, and, where possible, adding to, experimental facts.*

* The literature upon catalysis is extensive. An admirable survey of the subject and original references may be found in "Die Katalyse," by G. Woker, 645 pp. (1910). For a briefer review, see "Die Lehre von der Reaktionsbeschleunigung durch Fremdstoffe," by W. Herz. Ahrens' "Sammlung chemischer und chemisch-technischer Vorträge." For a still briefer review see Ostwald, *Zeitschr. f. Elektrochem.*, 7, 995–1004 (1901).

CHAPTER XXVI

EQUILIBRIA IN CHEMICAL REACTIONS

DEFINITIONS of the terms "reversible reaction" and "chemical equilibrium" are included in every course on general chemistry nowadays. The following experiment, or one similar to it, will probably be remembered as having been shown early in a beginning course. Pass a current of steam over hot copper and the water is to a certain extent decomposed, forming copper oxide and hydrogen. Pass a current of hydrogen over hot copper oxide and the oxide is reduced and some water is formed. The reaction is reversible and, adopting the suggestion of van't Hoff, we indicate this by substituting double arrows for the equality mark, writing, $H_2O + Cu \rightleftarrows CuO + H_2$.

Equilibrium the Same from whichever Side Approached. If water vapor and copper are heated in a sealed tube the reaction will proceed from left to right until definite concentrations (depending on the temperature) of water vapor and hydrogen are reached. If hydrogen and copper oxide are heated to the same temperature in a sealed tube, the reaction will proceed from right to left until precisely the same concentrations as in the previous case are reached. The system is in equilibrium with some of everything possible present, and the conditions are the same from whichever side approached.

After the first course in general chemistry is completed, qualitative, and perhaps quantitative, analysis is taken up. These subjects deal almost exclusively with reactions which go practically to completion. They are chosen precisely because they have this characteristic which is essential for the purpose of analysis. The student is an exception, or these subjects are exceptionally well taught, if he does not get the idea that the majority of chemical reactions go to completion, and that those which reach conditions of equilibrium are relatively few and unimportant. At the next stage of his chemical education, studying organic or physical chemistry, he must unlearn this and realize that the converse is true. The reactions of daily life, as we may call them, processes of growth of animals and vegetables, most of the reactions basic for great chemical industries such as the manufacture of sulphuric acid, alkalies, soap, etc., go but part way

and reach equilibrium with notable quantities of every possible compound present.

All Reactions Reversible. Careful study has shown that we can determine the equilibrium conditions in cases where, not many years ago, it was thought surely we had complete reactions. Coke does not burn completely to carbon dioxide in a blast furnace and equilibrium is reached with readily measurable quantities of carbon monoxide present. When hydrogen and oxygen are exploded to form water, at high temperatures we can still measure the quantities of hydrogen and oxygen which did not react but remain present in equilibrium with the water vapor. Add a solution of potassium ferrous oxalate to a solution of silver nitrate and silver is precipitated. Filter, and add a solution of sodium chloride to the filtrate. No silver chloride appears, and as this is so delicate a test for the presence of silver ions we may assume the reduction went to practical completion. But now add a solution of ferrous sulphate to a solution of silver nitrate and again silver is precipitated. Filter and test as before and the appearance of a precipitate of silver chloride proves that this reduction did not go to completion but reached a condition of equilibrium with readily perceptible quantities of silver ions still in solution. We have every reason to suppose that a sufficiently delicate test would have revealed the presence of silver ions in the previous case. Such illustrations might be multiplied almost without end and we feel justified in saying that no reaction goes to absolute completion. All reach conditions of equilibrium, though sometimes these conditions are so far to one side they, for all practical purposes, may be considered as complete. And, as a necessary corollary to this we say all reactions are reversible, to a certain extent at least. There is no such thing known as a completely irreversible reaction, therefore the old subdivision into reversible and irreversible reactions might as well be abandoned.

Formulation of Equilibrium. The law of mass action is our guide in the study of equilibrium conditions as it was in our study of velocities; indeed the formulation for equilibrium conditions follows immediately from those we developed in the last chapter. Consider the reaction, $A + B \rightleftarrows C + D$. If we start with A and B, the velocity of the reaction is $\frac{dx_1}{dt_1} = k_1 C_A C_B$ where C_A is the concentration of A and C_B is the concentration of B. If we start with C and D the velocity of the reaction is $\frac{dx_2}{dt_2} = k_2 C_C C_D$. The interaction of A and B producing C and D must start the reverse reaction; or,

if we began with C and D, A and B would be produced and the opposite reaction would begin at once. We have had occasion several times to say that chemical equilibrium is by no means a condition of rest but rather the condition where the opposed reactions have the same velocities.

"Balanced Action." This reasoning is the origin of the term "balanced action" which is but an alternative, and less good, name for equilibrium.

When equilibrium is reached $\frac{dx_1}{dt_1} = \frac{dx_2}{dt_2}$. If this is so then $k_1C_AC_B = k_2C_CC_D$. Transposing we have, $\frac{C_AC_B}{C_CC_D} = \frac{k_2}{k_1}$. As k_1 and k_2 are both constants we combine them and write K, a value known as the equilibrium constant.

This method of reasoning is entirely general. Applying it to the skeleton equation which includes all possible chemical reactions, $mA + nB + pC \ldots = qD + rE + sF \ldots$ as used in the last chapter, we have, $\frac{C_A{}^mC_B{}^nC_C{}^p \ldots}{C_D{}^qC_E{}^rC_F{}^s \ldots} = K$.

This formulation is our fundamental generalization from the study of homogeneous systems. It is, however, applicable also to heterogeneous systems wherein the phase law is the fundamental generalization. The formulation itself is so logical and simple it is easily learned and one hardly suspects at first its potentialities for explaining apparently most diverse phenomena. Appreciation of these potentialities grows with practice in its applications. All the rest of this chapter is devoted to showing how to apply it to typical cases.

Classification. It is convenient to divide our examples into three groups; first, heterogeneous physical equilibria; second, homogeneous chemical equilibria; third, heterogeneous chemical equilibria. All homogeneous equilibria are perforce chemical equilibria; heterogeneous equilibria may be either physical or a combination of physical and chemical.

Order of Equilibrium. When equilibrium exists in a system of one component it is said to be of the first order. If the system contains two components the equilibrium is said to be of the second order, and so forth. Equilibria are often considered according to this classification.*

* The number of new terms and new schemes of classification which it has been necessary to describe since we began Chapter XX is large; perhaps too large. It is certainly possible to over systematize a subject. Science is systematized

Heterogeneous Physical Equilibria. By chemical reaction we usually understand a change involving the appearance of one or more new chemical individuals. Processes which reach their conditions of equilibrium without the simultaneous appearance of new substances are called physical. It may be objected that they do not properly belong in a chapter devoted to chemical equilibrium. But it is worth while to show that the great generalization from all chemical reactions is applicable to these physical processes also, and to demonstrate, first, that they merge continuously into chemical processes and, second, the futility of trying to draw a dividing line between the two sciences. Indeed there are more real and important differences in the properties of a substance as a gas, as a liquid, and as a solid, than there are between sodium hydroxide and potassium hydroxide for instance.

Heterogeneous equilibrium must establish itself at the surface separating the phases, and therefore the equilibrium conditions are not altered by changes in the total quantities of the phases. We have dealt with a number of such equilibria already in our discussions of changes between conditions of aggregation and the process of solution. It remains now only to show that the law of mass action is applicable.

Equilibrium between Pure Liquid and its Vapor. Consider the equilibrium between a pure liquid and its vapor. According to the law of mass action the amount of vapor which condenses to a liquid per unit time is proportional to the concentration of the vapor, C_1, and the amount of liquid which vaporizes per unit time is proportional to the concentration of the liquid, C_2. The process is so much like a simple chemical change we may write it in the form of a reversible reaction, liquid $\rightleftarrows$ vapor. Then the velocity of the reaction from right to left is $\frac{dx_1}{dt_1} = k_1C_1$ and from left to right it is $\frac{dx_2}{dt_2} = k_2C_2$.

knowledge, therefore one is apt to fall into the error of thinking that the main object of science is to systematize and classify. It is not. Classification is merely a means to an end. The main object of science is to teach, and to fit men as rapidly as possible to acquire new knowledge or to apply the knowledge we have. All classification which tends to condense or make clearer what we know forwards these aims and is desirable. Classification which does not forward these aims is a not wholly harmless pastime, as it delays those anxious to do their share of the world's work. Multiplication of technical terms makes scientific treatises unintelligible to all but specialists. It is therefore greatly to be deplored that so many are indispensable, and we should at least endeavor to reduce their number as much as possible.

Equilibrium is reached when $\frac{dx_1}{dt_1} = \frac{dx_2}{dt_2}$, that is, when $k_1C_1 = k_2C_2$, or $\frac{C_1}{C_2} = \frac{k_2}{k_1} = K$. At any definite temperature the concentration of a pure liquid is a constant and so C_2 may be included in K and we have, $C_1 = K$. The concentration of a vapor is directly proportional to its pressure and so we have reached the familiar fact that at any definite temperature a liquid has a definite vapor pressure.

Equilibrium between a Gas and a Solution of that Gas. Consider the case of a gas dissolving in a liquid. We have the gas going into and coming out of solution, a species of chemical reaction. We may write, gas $\rightleftarrows$ gas dissolved. Let C_1 = concentration of the gas in solution and C_2 = concentration of the gas in the gaseous phase. Equilibrium will be reached when $k_1C_1 = k_2C_2$, or $\frac{C_1}{C_2} = \frac{k_2}{k_1} = K$. This shows that for any definite temperature the ratio between the concentration of the gas as such and the gas dissolved is a constant. This is simply Henry's law, discussed in Chapter XXIV.

Exceptions to Henry's Law. Henry's law does not apply to substances which may be supposed to combine chemically with the solvent as, for instance, ammonia. We believe that ammonia unites to a considerable extent with water according to the reaction, $NH_3 + H_2O = NH_4OH$. Doubtless the usual expression, $\frac{C_1}{C_2} = K$, does apply here too when C_1 equals the concentration in the gaseous phase and C_2 equals the concentration of the NH_3 still unchanged in the solution. The large observed solubility and the deviations from the law are thus logically accounted for by the reaction which removes one of the factors of the equilibrium. The same reasoning applies to solutions of hydrogen chloride and of all other gases whose solubilities are not formulated by the law. It is plausible to suppose they all enter into reaction with the solvent.

Inferences Regarding Association, Dissociation, etc. This reasoning is often used. When our formulæ, based on the law of mass action, do not hold, we infer that some reaction, perhaps not before suspected, has taken place. This may be association to larger molecular aggregates, dissociation to ions, or reactions resulting in the formation of new compounds, for any one of these processes alters the concentration of the substances taking part directly in the equilibrium.

Other Physical Equilibria. That the same reasoning may be carried out for other systems which we have studied, for a solid subliming and in equilibrium with its vapor, for the condensed system consisting of one substance as solid and liquid in contact and in equilibrium, for a solution in equilibrium with excess solute, etc., is so evident we need not spend time and space in the demonstrations. It will be more profitable to take up cases which offer new features. These appear when the equilibrium involves a chemical reaction.

Homogeneous Equilibrium in the Gaseous Phase. The standard illustration of equilibrium conditions in the gaseous phase is the reaction $H_2 + I_2 \rightleftarrows 2\,HI$. It is well adapted for investigation as it goes to equilibrium in a few hours at the temperature of boiling sulphur (448°), but proceeds exceedingly slowly at room temperature. Thus, by cooling quickly, the conditions prevailing at the higher temperature are continued long enough to determine analytically what they are. On this account it has been thoroughly investigated, first by Hautefeuille, then by Lemoine, and most recently and most accurately by M. Bodenstein.*

If C_1 is the concentration of the hydrogen, C_2 the concentration of gaseous iodine, and C_3 the concentration of the hydrogen iodide, then, according to the general equation for equilibrium,

$$\frac{C_1 C_2}{C_3^2} = K.$$

Bodenstein sealed known quantities of hydrogen and iodine in glass bulbs, heated these in the vapor of boiling sulphur until equilibrium was reached, cooled and determined the quantities of iodine and hydrogen iodide by titration, and of hydrogen by measuring the volume. Expressing all quantities in chemical units (molecular weights or fractions of molecular weights in grams), let the original amount of hydrogen equal b, of iodine equal a, and let $2y$ equal the amount of hydrogen iodide formed. Then $b - y$ is the amount of hydrogen and $a - y$ is the amount of iodine gas present when equilibrium is reached. The concentrations are directly proportional to the amounts present and so we may substitute these values for C_1, C_2, and C_3 in the fundamental equation. We then obtain: $K = \frac{(b-y)(a-y)}{4y^2}$. Solving this equation for y we obtain

$$2y = \frac{a + b - \sqrt{a^2 + b^2 - ab(2 - 16K)}}{1 - 4K}.$$

* *Zeitschr. f. phys. Chem.*, **22**, 1–32 (1897).

As equal volumes of all gases under the same conditions may be assumed to contain the same number of molecules, we may substitute volumes for a, b and y. Bodenstein therefore expressed his results in cm³ (calculated to 0° and 760 mm.). He found that at 448° $K = 0.019\,84$ and at 350° $K = 0.014\,94$. Inserting these values and his analytical data, in the formula, he calculated the number of cm³ HI he should have and compared these numbers with the cm³ HI which he actually found. The following table contains a few of his results obtained with different initial quantities of hydrogen and of iodine. The calculated values agree well with those actually found and so furnish us with good evidence that our reasoning is correct.

HI PRESENT AT 448°.

Hydrogen. b	Iodine. a	HI calculated. $2y$	HI found.
20.57	5.22	10.19	10.22
20.60	14.45	25.54	25.72
15.75	11.90	20.65	20.70
14.47	38.93	27.77	27.64
8.10	2.94	5.64	5.66
8.07	9.27	13.47	13.34

A similar table showing equally good agreements at 350° is omitted to save space.

Effect of Pressure when the Reaction Does not Alter the Volume. In the example we are considering we may substitute the partial pressures of the three gases for their concentrations in the equilibrium equation, for these partial pressures are directly proportional to the concentrations. Let p_1 equal the partial pressure of the hydrogen, p_2 that of the iodine, p_3 that of the hydrogen iodide. We then have $\frac{p_1 p_2}{p_3^2} = K$. If we double the total pressure this doubles each partial pressure and we have $\frac{2\,p_1\,2\,p_2}{4\,p_3^2} = K$. Canceling we obtain the original expression unaltered.

We may alter the pressure on the system as we please, let us say making it n times what it was originally. Then the partial pressures are all altered to the same extent and we have $\frac{np_1np_2}{n^2p_3^2} = K$. n cancels out and we have the original expression again. The equilibrium conditions are then independent of the pressure. This is true only for cases wherein the reaction involves no change in volume.

Effect of Pressure when the Reaction Alters the Volume. If, however, we are dealing with a reaction which involves a change in volume, as for instance when N_2O_4 dissociates to $2\,NO_2$ according to the reaction $N_2O_4 \rightleftarrows 2\,NO_2$, a change in pressure does alter the equilibrium conditions.* Let p_1 equal the partial pressure of N_2O_4 and p_2 the partial pressure of NO_2. Then $K = \frac{p_2^2}{p_1}$. Suppose the total pressure be made n times the original, then $K = \frac{n^2p_2^2}{np_1} = \frac{np_2^2}{p_1}$ and n does not cancel out. It is seen at once from this formula that if we increase the total pressure on the system this must diminish the quantities of the dissociation products and that a decrease in pressure must increase them.

In Chapter XII we learned to calculate the degree of dissociation of a gas from its vapor density and derived the formula $\alpha = \frac{\delta - \Delta}{\Delta(n-1)}$, where α = fraction dissociated, n = number of molecules resulting from the dissociation of one molecule, δ = vapor density of not dissociated gas, and Δ = observed vapor density of the mixture. In the case of N_2O_4, $n = 2$, and we have $\alpha = \frac{\delta - \Delta}{\Delta}$. If we enclose a known weight of N_2O_4 in a tube of known volume, raise it to temperature, t, and measure the pressure of the gaseous mixture, p, we have all the data necessary to calculate, with the assistance of the gas laws both Δ and δ. Thus it is easy to determine experimentally how much of the original substance and how much of the products are present when equilibrium is reached.

Dissociation Constant. According to the general expression for equilibrium, if C_1 = concentration of N_2O_4 and C_2 = concentration of NO_2, $\frac{C_2^2}{C_1} = K$. As these substances are gases the concentrations are proportional to the amounts present. The amount of N_2O_4 is $1 - \alpha$ and of NO_2 is α, therefore $\frac{\alpha^2}{1-\alpha} = K$. Experiments demonstrate that the actual facts correspond to this reasoning and formulation. This K, the equilibrium constant, is, in this connection, called the dissociation constant.

Effect of the Presence of One of the Products of Dissociation. For the equilibrium, $PCl_5 \rightleftarrows PCl_3 + Cl_2$, letting p_1 equal the partial

* Investigated by Natanson, *Wied. Annal.*, **24**, 454 (1885); and **27**, 606 (1886).

pressure of PCl_3, p_2 that of the Cl_2, and p_3 that of the PCl_5, we have the formulation, $\frac{p_1 p_2}{p_3} = K$.

Suppose that we add chlorine to the system. This increases the value p_2, then p_1 must diminish and p_3 must increase accordingly because, at any one temperature, K remains constant. The effect would be the same if we added phosphorus trichloride, thus increasing the value of p_1. Then adding either product of the dissociation diminishes the amount of the dissociation which occurs before equilibrium is reached.

Homogeneous Equilibrium in Liquids. Berthelot and Pean de St. Gilles studied the formation and saponification of various organic esters and determined the equilibrium conditions before Guldberg and Waage put the law of mass action in mathematical form.* To take one example, we may express the equilibrium between ethyl acetate and water on the one hand, and ethyl alcohol and acetic acid on the other, as follows: $CH_3COOC_2H_5 + H_2O \rightleftarrows C_2H_5OH + CH_3COOH$. Let C_1 equal the concentration of ethyl acetate, C_2 that of water, C_3 that of alcohol, and C_4 that of acid, all in gram-molecular weights, then we have, $\frac{C_1 C_2}{C_3 C_4} = K$.

If equimolecular quantities of ethyl alcohol and acetic acid are enclosed in a sealed tube and heated to 150° for a few hours equilibrium is reached. The tube may then be cooled, opened, and the contents analyzed, for the reaction proceeds very slowly at room temperature. Moreover it has been found by experiment that the equilibrium conditions are but slightly different at different temperatures. Such analysis shows equilibrium exists between one-third of a molecular weight in grams each of acetic acid and alcohol, and two-thirds of a molecular weight in grams of the ester and water respectively. If we start with a molecular weight in grams of the ester and of water, treat the system similarly and analyze, we find the same quantities of the four substances. Tubes have been kept seventeen years before opening and then proved to contain these quantities. This is experimental evidence of the fact, to be remembered, that equilibrium conditions are the same from whichever side approached.

Inserting these numerical values in our formula we have,

$$\frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = K = 4.$$

* Berthelot and Pean de St. Gilles, *Ann. de Chim. et de Phys.* (3), **65**, 385; **66**, 5 (1862); **68**, 225 (1863).

Utility of the Formulation. The significance of what we have here achieved should be fully realized. The formula and the equilibrium constant enable us to foretell what the effect will be of altering the concentrations of either of the reacting substances or of having some of the products present. They enable us to calculate quantitatively what our yield will be under given conditions and so tell us what we must do to accomplish a given end. All of these questions are eminently practical and an ability to apply these fundamental principles has more than once converted a loss to a profit in the factory.

The formula shows that if we increase the concentration of the water (C_2) the concentration of the ester (C_1) must diminish, and that of the alcohol (C_3) and that of the acid (C_4) must increase, for the fraction as a whole will remain equal to 4. If one is manufacturing the ester this is an undesirable thing to do; if the ester is being saponified in order to get the alcohol or acid, it is a desirable thing to do. If some agent is introduced to remove water almost as fast as formed this will increase the yield of ester, because much more alcohol and acid must disappear, *i.e.*, enter into reaction, forming more ester. We have here the underlying reason for the well-known rule — to cause a reaction to proceed to practical completion remove one of the products as fast as formed.

Quantitative Calculation. The following will serve as an illustration of the way to carry out a quantitative calculation of the results. Let us suppose that we intend to make ester from alcohol and acid and wish to know what yields of ester to expect starting with different quantities of our substances.

Let m = molecular weights of alcohol and n = molecular weights of acid used. Let x = molecular weights of alcohol which react. Then x = molecular weights of acid which react, molecular weights of ester which are formed, and also molecular weights of water which are formed. Then $m - x$ = molecular weights of alcohol left, and $n - x$ = molecular weights of acid left when equilibrium is reached. Let v = volume of the whole system. Then

$$\frac{x}{v} = C_1, \frac{x}{v} = C_2, \frac{m-x}{v} = C_3, \frac{n-x}{v} = C_4.$$

Substituting these values in the fundamental equation we have,

$$\frac{\frac{x^2}{v^2}}{\frac{(m-x)(n-x)}{v^2}} = K = \frac{x^2}{(m-x)(n-x)} = 4.$$

Solving this equation for x we obtain,

$$x = \frac{2}{3}(m+n) \pm \frac{2}{3}\sqrt{m^2 - mn + n^2},$$

which tells us at once how the yield of ester (x) varies according to the initial quantities of alcohol (m) and acid (n). For instance, if we begin with a molecular quantity of each, $m = 1$ and $n = 1$. Substituting these values we have $x = \frac{4}{3} \pm \frac{2}{3}$, *i.e.*, $x = 2$ or $\frac{2}{3}$. We are never at a loss as to which of the two roots to select as it would be quite absurd to suppose we could obtain a quantity of ester more than equivalent to either of the necessary reagents. Therefore the answer is not 2 but $\frac{2}{3}$, which agrees with the experimental results already given.

If we begin with two molecular quantities of alcohol to one of acid, $m = 2$ and $n = 1$. Substituting we find x (the yield of ester) is $2 \pm \frac{2}{3}\sqrt{3}$, *i.e.*, 3.162 or 0.838. We discard the first as impossible and so 0.838 molecular weights of ester will be obtained.

If we begin with four molecular quantities of alcohol to one of acid, $m = 4$ and $n = 1$. Substituting we find we shall obtain 0.930 molecular-weight quantities of ester.

If we begin with two molecular quantities of alcohol and six of acid, $m = 2$ and $n = 6$. Substituting we find the yield of ester to be 1.805 molecular weights.

The student should practice on other examples, for by such calculations alone will he grow to appreciate the great possibilities and practical value of these fundamental principles.

Effect of Adding One of the Products of the Reaction. In case some of one of the products is present to begin with the formula becomes a little more complicated, but not in the least more difficult to understand. For example, suppose q molecular weights of water are present to begin with, then when equilibrium is reached the concentration of the water present is $\frac{x+q}{v}$. This makes the fundamental formula read: $\frac{x(x+q)}{(m-x)(n-x)} = 4$. Solving for x we get the somewhat cumbersome expression:

$$x = \frac{1}{6}(4n + 4m + q \pm \sqrt{16n^2 - 16mn + 8nq + 8mq + 16m^2 + q^2}).$$

These formulæ have been tried experimentally, not only upon the

formation of esters, but on numerous other reactions whose fundamental formulations are the same, and they have been found to fit the facts.

Effect of Change in Volume. In the esterification $\rightleftarrows$ saponification example just discussed the term representing the volume canceled out and therefore changing the volume of the system could not alter the equilibrium conditions. But this term does not always cancel out. The decomposition of amyl acetate reaches an equilibrium represented by $CH_3COOC_5H_{11} \rightleftarrows CH_3COOH + C_5H_{10}$. Suppose we mix unit quantity of the acid with a unit quantities of amylene, that v is the volume of the mixture and that x unit quantities of amyl acetate are formed when equilibrium is reached. At that time we shall have $1 - x$ acid and $a - x$ amylene present. If C_1 represents the concentration of the amylene, C_2 that of the acid, and C_3 that of the ester, then $\frac{C_1C_2}{C_3} = K$. The concentration of the amylene is $\frac{a-x}{v}$, of the acid $\frac{1-x}{v}$, of the ester $\frac{x}{v}$. Substituting we have,

$$\frac{\frac{a-x}{v} \times \frac{1-x}{v}}{\frac{x}{v}} = K, \text{ or } \frac{(a-x)(1-x)}{vx} = K.$$

Konowalow* and Nernst and Hohmann† have investigated this equilibrium and have proved that the experimental facts correspond to this formulation. Notice that, K being a constant, if we hold a constant and increase v, x must decrease. In words this tells us that the larger the volume (the greater the dilution) the less the quantity of ester formed.

Homogeneous Equilibrium in Solutions. Homogeneous equilibria in solutions include some of the most interesting and important applications of the law of mass action. According to the dissociation theory, when we dissolve common salt in water some of it dissociates until we have equilibrium between the undissociated substance and its ions. We may represent this equilibrium as $Na^{\cdot} + Cl' \rightleftarrows NaCl$. If C_1 = concentration of $Na^{\cdot}$, C_2 = concentration of Cl', and C_3 = concentration of NaCl, $\frac{C_1C_2}{C_3} = K$. Suppose we start with unit quantity of NaCl and that α is the fraction dissociated

* *Zeitschr. f. phys. Chem.*, 1, 63–67 (1887); 2, 6–12, 380–389 (1888).

† *Ibid*, 11, 352–390 (1893).

when equilibrium is reached. Then $1 - \alpha$ is the quantity of undissociated NaCl and α is the quantity of sodium ion and also of chloride ion present. Let v = total volume of the system. Then $\frac{1-\alpha}{v}$ = concentration of NaCl, $= C_3$, $\frac{\alpha}{v}$ = concentration of $Na^{\cdot} = C_1$ = concentration of $Cl' = C_2$. Then

$$\frac{\frac{\alpha^2}{v^2}}{\frac{1-\alpha}{v}} = K = \frac{\alpha^2}{v(1-\alpha)}.$$

Ostwald's Dilution Law.* The equilibrium constant, K, in the above formula is called the dissociation constant, and the formula, showing, as it does, the relation between the degree of dissociation and the degree of dilution, is known as Ostwald's dilution law. The degree of dissociation, α, may be determined with ease, either by application of the boiling-point or freezing-point method as has been described, or more conveniently by the conductivity method which will be described in Chapter XXVIII.

The validity of the formula was tested by Hoff and Reicher † with a number of substances. The following table contains their results with acetic acid at 14.1°. They used the conductivity method and inserting one experimental value for α calculated the dissociation constant, $K = 0.000\,018$. They then compared their other experimentally determined values for α with those calculated, assuming $K = 0.000\,018$ a constant as required by the formula. The first column (v) contains the number of liters in which there was one molecular weight in grams, the second (α_1) the per cent dissociation experimentally found, the third (α_2) the per cent dissociation calculated according to the formula.

v	α_1	α_2
0.994	0.402	0.42
2.02	0.614	0.6
15.9	1.66	1.67
18.1	1.78	1.78
1 500	14.7	15.0
3 010	20.5	20.2
7 480	30.1	30.5
15 000	40.8	40.1

* *Zeitschr. f. phys. Chem.*, **2**, 270–283 (1888).
† *Ibid*, **2**, 777–781 (1888).

There is here an admirable correspondence between the deduction and the facts.

An Empirical Formula for Strongly Dissociated Substances. But the formula does not hold so well for strongly dissociated substances and it has been suggested that, since we can hardly call the law of mass action into question, the mechanism of electrolytic dissociation may not be just as we imagine it in these cases.

M. Rudolphi * suggested and van't Hoff † improved a purely empirical formula which appears to correspond with the facts for strongly dissociated substances. This is, $\frac{\alpha^3}{v(1-\alpha)^2} = K$.

In the following table, under K_1 are values for the dissociation constant of silver nitrate (25°) calculated according to Ostwald's dilution law, under K_2 values calculated according to the Rudolphi-van't Hoff formula.

v	K_1	K_2
16	0.26	1.11
32	0.19	1.16
64	0.13	1.06
128	0.091	1.07
256	0.064	1.08
512	0.048	1.09

The inconstancy of K_1 and the constancy of K_2 are apparent.

Color of Ions. A dilute solution of sulphuric acid is colorless. We assume it to be partly dissociated and to contain $H^{\cdot}$, HSO_4' and SO_4'' as ions. Therefore these ions must be colorless. A dilute solution of $CuSO_4$ is practically completely dissociated to $Cu^{\cdot\cdot}$ and SO_4'' and it is blue. Therefore the copper ion must be blue. This conclusion is reënforced by the fact that dilute solutions of other copper salts are blue.

The following is a convenient lecture experiment to show qualitatively that dissociation increases upon dilution. A solution of HCl is colorless, therefore both ions are colorless. A concentrated solution of cupric chloride is green. This must be the color of undissociated $CuCl_2$. Add water gradually and the green changes to blue, *i.e.*, we can see that we have less and less of the undissociated $CuCl_2$ and more and more of the copper ion. That this effect is a necessary

* *Zeitschr. f. phys. Chem.*, 17, 385–426 (1895).
† *Ibid*, 18, 300–304 (1895).

corollary from the law of mass action can be made clear in the most elementary classes by a simple arithmetical example based on an electrolyte which dissociates into two ions. If C_1 = concentration of anion, C_2 = concentration of cation, and C_3 = concentration of the undissociated substance, then $\frac{C_1C_2}{C_3} = K$. This is the same as $C_1C_2 = KC_3$. Suppose that at the beginning the concentrations are such that one liter contains 8 undissociated molecules and 8 ions of each kind. The molecules plus the ions are equivalent to 16 molecules. Then $8 \times 8 = 8K$ and $K = 8$. To one liter of this solution add one liter of water. The molecules plus the ions in one liter must now be equivalent to 8 molecules and K, the constant, must remain equal to 8. Then $C_1C_2 = 8C_3$, $C_1 = C_2$, and $C_1 + C_3 = 8$. Solving these simultaneous equations we find $C_1 = 4.94$, $C_2 = 4.94$, and $C_3 = 3.06$. Making a series of these calculations we obtain the following table:

Liters.	C_1	C_2	C_3	
1	8	8	8	One molecule to 2 ions
2	4.94	4.94	3.06	One molecule to 3.22 ions
4	2.93	2.93	1.07	One molecule to 5.46 ions
8	1.66	1.66	0.34	One molecule to 9.79 ions
16	0.90	0.90	0.10	One molecule to 18 ions
etc.				

Numerical Values of Dissociation Constants. The following is a table containing the numerical values of the dissociation constant for some familiar acids and bases.

	K
Formic acid	0.000 214
Acetic acid	0.000 018 0
Propionic acid	0.000 013 4
Glycollic acid	0.000 152
Chloracetic acid	0.001 55
Trichloracetic acid	1.21
Benzoic acid	0.000 060
Salicylic acid	0.001 02
p-oxybenzoic acid	0.000 028 6
Ammonium hydroxide	0.000 023
Methylamine	0.000 50
Benzylamine	0.000 024
Aniline	0.000 000 000 11

Strength of Acids. Too frequently one hears the term strong acid when concentrated acid is meant. We should take particular

pains to use these terms in their correct meanings and so avoid unnecessary confusion. In physical chemistry, at least, by the strength of an acid we mean a property inherent in the nature of the substance. To find which is the stronger, we compare acids of the same concentration, both in equivalent normal or both in one-tenth equivalent normal solution, for instance. Having a series of acids of the same concentration, we may allow equal volumes to act on equal areas of a metal at a constant temperature. That acid which will dissolve most metal per unit time is properly called the strongest acid. If we determine the electrical conductivity of these equivalent solutions we shall find that that solution which dissolved the metal fastest conducts electricity best. The two methods of comparison put the acids in the same order. We have excellent reasons for supposing that the electrical conductivity is a measure of the dissociation. Therefore we say the strongest acids are those most dissociated. This is one of numerous reasons we have for ascribing all acid properties to the presence of the hydrogen ion. Then of course the characteristic effects of acids are more pronounced the greater the concentration of the hydrogen ion.

The greater the dissociation constant the greater the dissociation at a given dilution and so the dissociation constant of an acid is a numerical expression of its strength.

It was explained in the last chapter that the velocity with which sugar is inverted is directly proportional to the concentration of the hydrogen ion present. Therefore, adding equal volumes of equivalent solutions of acids and observing the resultant velocity of the inversion of sugar is another method of comparing the strength of acids.

Division of a Base between Two Acids. Suppose we have equivalent quantities of two acids in solution and add a base, but not enough to neutralize both. The acids will compete for the base, and the stronger acid will get more than the weaker. We have several experimental methods for determining how a base divides itself under such circumstances. For instance: when equivalent quantities of the base and one acid are mixed there is a change in volume; call it a. When equivalent quantities of the base and the second acid are mixed there is a different change in volume; call it b. When equivalent quantities of both acids are present and one equivalent quantity of the base is added there is a volume change c, which lies between a and b. If c is nearer a than b, evidently the first acid got more of the base than the second. If c is nearer b than

a then the second acid got the greater part of the base. By this method also we can then arrange acids in the order of their strengths.*

Affinity Constants. All three methods put the acids in the same order. In the following table, in column 1, are results obtained by determining how a base divides itself between two acids; in column 2 are results obtained by determining the velocity of sugar inversion; in column 3 are results obtained by determining the electrical conductivity (dissociation constant). In order that the values shall be directly comparable, in every case the value corresponding to the strongest acid is put equal to one hundred and all other values are reduced to the same standard.

	1	2	3
Nitric acid	100	100	100
Hydrochloric acid	98	100	99.6
Sulphuric acid	49	73.2	65.1
Trichloracetic acid	80	75.4	62.3
Dichloracetic acid	33	27.1	25.3
Monochloracetic acid	7	4.8	4.9
Oxalic acid	26	18.6	19.7
Succinic acid	1.5	0.55	0.58
Tartaric acid	5.0	.....	2.28
Citric acid	5.0	1.73	1.66
Formic acid	3.9	1.53	1.68
Acetic acid	1.23	0.40	0.42

These values are called affinity constants. While the numbers are by no means identical, with one exception the acids arrange themselves in the same order, whichever one of these methods is used to determine the affinity constants.

The significance of the table is further increased by the fact that the catalytic method has been used, not only with sugar inversion, but also with the saponification of methyl acetate into acetic acid and alcohol, with the conversion of acetamide into ammonium acetate, and with the rate at which calcium oxalate is dissolved, and it always puts these acids in the same order.

* Other methods: Heat of neutralization of acid No. 1 with the base = *a*. Heat of neutralization of acid No. 2 with the same base = *b*. Upon adding an equivalent quantity of base to a mixture containing an equivalent quantity of both No. 1 and No. 2 we find a heat of neutralization *c*, lying between *a* and *b*. From these values it is possible to determine the distribution of the base. Determination of the specific refractions of the several solutions will also furnish numerical values which may be utilized for the calculation.

Affinity Constants of Bases. What has been said regarding acids applies to bases with the single alteration that we believe they owe their characteristic properties to the presence of the hydroxide ion, OH′, and the strongest base is that which, being most dissociated, gives the greatest concentration of this ion. The rate at which equivalent quantities of different bases will saponify ethyl acetate furnishes experimental data which enable us to ascribe to them the following affinity constants.

Sodium hydroxide	100
Potassium hydroxide	100
Lithium hydroxide	102
Thallium hydroxide	91
Tetraethylammonium hydroxide	81
Ammonium hydroxide	2
Ethylamine	12
Diethylamine	16
Triethylamine	14

Affinity Constants in Other Solvents than Water. It is interesting that the affinity constants of the ammonium bases when dissolved in aniline, a solvent in which we have reason to believe there is very little dissociation, come out in just the same order as in water.*

In other solvents than water the order of affinities of the acids is sometimes different from that just given. These are interesting and perhaps significant facts but there is not yet sufficient unanimity as to their interpretation to justify their discussion in a book of the scope of this.

Effect of Adding More of One Ion. If we have a solution of a binary electrolyte (by which we mean a substance which, upon dissociation, gives two ions) in equilibrium, and increase the concentration of one of the ions, this must diminish the fraction dissociated. This is evident from the formula $\frac{C_1C_2}{C_3} = K$, for increasing the numerical value of C_1, the value of C_2 must diminish and the value of C_3 must increase as K is constant. We can increase the concentration of one ion by adding a concentrated solution of a second electrolyte which, upon dissociation, gives an ion the same as one already present. The applications of this principle are numerous. Let us consider a few of them.

* Goldschmidt and Salcher, *Zeitschr. f. phys. Chem.*, **29**, 89–118 (1899).

Qualitative Experiments. The following is a simple qualitative demonstration of the principle. Make a solution of cupric chloride of such concentration that it is neither blue nor green, and divide it between three test tubes. Add a few drops of concentrated HCl solution to one and it at once becomes greener. The addition of the HCl much increased the concentration of the Cl' and so drove back the dissociation of the $CuCl_2$ and we observed the green color characteristic of the undissociated $CuCl_2$.

To another portion add a solution of mercuric nitrate. The color becomes more distinctly blue. Some $HgCl_2$ is formed and this, being but slightly dissociated, results in a diminution of the concentration of the Cl' and this reduction is immediately followed by the dissociation of some more $CuCl_2$, *i.e.*, an increase in the concentration of the Cu''.

Quantitative Application. The application of this principle was first quantitatively proved by Arrhenius.* He measured the velocity of inversion of sugar when a certain concentration of acetic acid was present. He then added sodium acetate and found the velocity was much diminished. As has been stated several times, the velocity with which sugar is inverted is directly proportional to the concentration of the hydrogen ion present. Sodium acetate has the same anion as acetic acid and increasing its concentration must then have diminished the dissociation of the acetic acid and so the concentration of the hydrogen ion. From the velocities Arrhenius calculated these concentrations and found they corresponded with those calculated by the equilibrium formula.

Reduction of Acidity by the Addition of a Neutral Salt. It often happens, particularly in analytical processes, that we wish to have a solution just barely acid. We may produce this condition by adding a small quantity of an acid, or we may diminish the concentration of the hydrogen ion already present by adding to the solution a neutral salt of that same acid. The concentration of the anion is thus increased and the dissociation of the acid correspondingly diminished.

We may reduce the basicity of a solution in the same way. Suppose the solution contains a quantity of a weak (relatively little dissociated) base. We add a solution of a salt which, upon dissociation, gives the same cation as the base. Thus increasing the concentration of the cation drives back the dissociation of the base and

* *Zeitschr. f. phys. Chem.*, **5**, 1–22 (1890).

diminishes the concentration of the OH' to which the base owes its characteristic properties.

Hydrolysis. Sodium carbonate in water solution gives an alkaline reaction, ferric chloride in water solution gives an acid reaction, potassium cyanide in water solution gives an alkaline reaction and smells of hydrocyanic acid. Many such cases are known. The most plausible explanation is that these substances enter into reaction with the water, giving new substances not originally present. We say they have undergone hydrolysis.

Water is supposed to be slightly dissociated; according to Kohlrausch's measurements 11 000 000 liters of water at 18° contain one formula weight of hydrogen ion and one formula weight of hydroxide ion. Equilibrium exists between the ions and the not dissociated substance and if we denote the concentration of the $H^{\cdot}$ with C_1, that of the OH' with C_2, and that of the undissociated water with C_3 we have $\frac{C_1 C_2}{C_3} = K_1$, and K_1 is an exceedingly small quantity.

When we dissolve one of these substances we also have equilibrium between it and its ions. Let us develop the reasoning using potassium cyanide solution as an example. We have $\frac{C_{K} \cdot C_{CN'}}{C_{KCN}} = K_2$, and K_2 is a large quantity for KCN is much dissociated.

Now, in the solution, we have hydrogen ion due to the water and cyanide ion (CN') due to the salt. According to the generally accepted idea, anything that can form will form until a condition of equilibrium is reached. Therefore some not dissociated hydrocyanic acid forms and we have $\frac{C_{H} \cdot C_{CN'}}{C_{HCN}} = K_3$. The value of K_3 is small for hydrocyanic acid is a weak acid and but little dissociated.

The removal of the hydrogen ions and of cyanide ions in this way to form undissociated hydrocyanic acid diminishes the concentrations of these ions and upsets the other two equilibria, necessitating the dissociation of more water and of more potassium cyanide. This increases the concentrations of the potassium ion and of the hydroxide ion and gives us, in effect, a solution of potassium hydroxide, for that substance on dissolving we assume dissociates to potassium ion and hydroxide ion.

We may express this as a reaction:

$$K^{\cdot} + CN' + H^{\cdot} + OH' = K^{\cdot} + OH' + HCN,$$

which makes evident the plausibility of the explanation.

The acid reaction of ferric chloride for instance is equally simply explained. Ferric hydroxide is a weak base, but little dissociated. Hydrolysis produces not dissociated ferric hydroxide and free hydrochloric acid, hence the acid reaction. We may write:

$$Fe''' + 3\,Cl' + 3\,H' + 3\,OH' = Fe(OH)_3 + 3\,H' + 3\,Cl'.$$

Theory of Indicators. An indicator, as is well known, is a substance which undergoes a marked color change when the solution containing it changes from acid to alkaline, or the converse. Litmus, phenolphthaleïn, and methyl orange are three of the most used indicators, but over a hundred different substances may be so used. These indicators are rather weak acids or bases, that is, but slightly dissociated in water solution; their K values are small numbers. In order to be useful as an indicator, the anion in case of an acid, or the cation in case of a base, must be intensely colored; or, more generally, there must be a marked color difference between the solution of the undissociated substance and the solution containing its ions.

Let us develop the reasoning using phenolphthaleïn as an illustration. In acid solution this is colorless, in alkaline solution it shows the familiar brilliant red. Phenolphthaleïn is a very weak acid which we may represent by HA. HA is colorless, H' is colorless, but A' is an intense red. In neutral solution the concentration of A' is so very small we do not see it, nevertheless equilibrium exists which we may represent by $HA \rightleftarrows H' + A'$. Adding an acid increases the concentration of the H' and drives the dissociation of HA yet further back. Adding an alkali increases the concentration of the OH' always present in at least minute quantities due to the slight dissociation of water. Now in every solution some of everything possible must be present and every equilibrium must be satisfied. Hydrogen ions are present due to the slight dissociation of the phenolphthaleïn, and if hydroxide ions are introduced they must combine with the H' ions to form not dissociated water. This upsets the equilibrium represented in the reaction and more HA must dissociate. The H' so added may combine with more OH' until a new equilibrium establishes itself. This new equilibrium corresponds to a much larger concentration of A' and so we see the characteristic red color.

This method of regarding indicators also gives us plausible reasons for their unsatisfactory behavior under certain circumstances and, what is more useful, enables us to select the indicator best suited for a given titration. We have learned from countless experiments that

salts of either strong acids or strong bases, or both, are much dissociated, while salts of weak acids with weak bases are but slightly dissociated. Now if we add some ammonium hydroxide (a weak base, see table of dissociation or affinity constants on p. 388) to phenolphthaleïn, we obtain the characteristic bright red color. In this solution we have $H^{\cdot}$, $NH_4^{\cdot}$, OH', and A' ions and undissociated HA, NH_4OH, and NH_4A. One equilibrium exists between $NH_4^{\cdot}$ and A' on the one hand and NH_4A on the other, and it is such that a perceptible quantity of A' is present. If to this solution we add some NH_4Cl the color disappears. According to our theory this increases the concentration of the $NH_4^{\cdot}$ which pushes back the dissociation of NH_4A, thus removing A' from the solution until its color is no longer perceptible.

The salt NH_4A is so slightly dissociated that hydrolysis occurs giving NH_4OH and HA, so there must be some little excess NH_4OH present before the characteristic color shows. Thus the " end point " does not appear at the right place and we can see why this indicator is not suited for use in titrations of, or with, NH_4OH.

If we have to titrate a weak base such as NH_4OH we should use a stronger acid than phenolphthaleïn as an indicator. Paranitrophenol is a stronger acid, colorless as such or in acid solution; its anion is a greenish yellow. Its ammonium salt, being a salt of a stronger acid than phenolphthaleïn, is less hydrolyzed and so the " end point " comes more nearly where it should.

We may generalize from these facts. When we have to titrate a weak acid or base we must use as indicator a stronger acid or base than is otherwise necessary. Of course we must not use too strongly dissociated a substance either, for then we should have the color change too far the other side of the true end point.

A thorough discussion of only the most used indicators would require more space than we can afford to give it Enough has been said to show how their behavior may be interpreted in the light of the law of mass action and our equilibrium formulæ.

Recent investigations cast doubt on the applicability of the dissociation theory to some indicators.* In several cases it seems more reasonable to suppose that the color change is due to a change in the structure of the molecule of the indicator. But whether this be so or not in no wise alters the applicability of the law of mass action. In place of an equilibrium between a not dissociated substance and

* See, for example, J. Stieglitz, *Jour. Am. Chem. Soc.* **25**, 1112–1127 (1903).

its ions we have only to substitute equilibrium between molecules of one structure and those of another.*

Homogeneous Equilibrium in a Solid Phase. Since we have solid solutions it is reasonable to suppose reactions occur and reach conditions of equilibrium in one homogeneous solid phase. Owing to the slowness of diffusion, however, it would be very difficult to measure the velocity of such reactions. Spring † found that equimolecular quantities of solid barium carbonate and sodium sulphate reacted upon being shaken together (much faster under high pressures) and reached equilibrium when about four-fifths of the barium carbonate had become barium sulphate. Starting with barium sulphate and sodium carbonate, about one-fifth of the barium sulphate became barium carbonate. In other words the same equilibrium conditions were reached from either side.

Transformations, changes from one crystal form to another, and the gradual crystallization of an amorphous solid may be considered as heterogeneous reactions which may result in equilibria between two solid phases.

Chemical Equilibria in Heterogeneous Systems. Let us now consider a few instances of equilibrium in heterogeneous systems. Whether they should be called physical or chemical, or a combination of the two, is of minor importance for the underlying principle is always the same.

Equilibrium between a Saturated Solution and an Excess of the Solid. When we make a solution of common salt we consider that equilibrium exists between the ions and undissociated salt. If C_1 is the concentration of the cations, C_2 the concentration of the anions and C_3 the concentration of the undissociated salt, $C_1C_2 = K_1C_3$. If the solution is saturated and an excess of the solid is present we have a second equilibrium and imagine that solid salt is dissolving at the same rate that undissociated salt is precipitating. If C_4 is the concentration of solid salt, then $C_3 = C_4K_2$. Since the concentration of a solid is a constant, $C_3 = K_3$. C_3 cannot then exceed a definite maximum. Anything which would tend to increase C_3 above this maximum must cause a precipitation of solid salt. Anything which would tend to diminish C_3 must result in more of the solid dissolving.

* For a full discussion of indicators, the various theories, and numerous references to the voluminous literature see "Der Stand der Indikatorfrage," by A. Thiel or Ahrens' "Sammlung Chemischer und chemisch-technischer Vorträge," Vol. 16, pp. 307–422 (1911).

† *Bulletin de la Société Chimique*, **46**, 299 (1886).

Solubility Product. Since there is a maximum value for C_3 and K_1 is a constant, there is a maximum value which the product of the concentrations of the ions can assume without causing precipitation. This maximum value is called the solubility product.

This simple reasoning furnishes us with satisfactory explanations of a number of well-known phenomena and has value in that it indicates how we may cause precipitation or solution to occur as desired. Let us illustrate this with a few definite examples.

The Solid which Precipitates First. If we mix solutions we consider that we have some of every possible substance in the resultant solution.* For instance, if we mix a solution of common salt and a solution of potassium nitrate, we consider that we have, not only undissociated NaCl in equilibrium with its ions and KNO_3 in equilibrium with its ions, but also KCl and $NaNO_3$ in equilibrium with their ions. Upon evaporation that solid will precipitate first whose solubility product is first reached. This is the only plausible explanation we have of the fact that we do actually obtain the same results whether we make the original solutions from NaCl and KNO_3 or from KCl and $NaNO_3$.

When we add a solution of $AgNO_3$ to a solution of NaCl, AgCl precipitates. We say that of all possible solids this has the smallest solubility product; its numerical value is so small it is almost sure to be exceeded. But we may make the solution so dilute that precipitation does not occur, and it is in fact solely a question as to whether the solubility product is exceeded or not.

Mixing Solutions with a Common Ion. Make equivalent solutions of $BaCl_2$ and of Na_2SO_4 of such dilution that upon mixing equal volumes, $BaSO_4$ just fails to precipitate. To a portion of the mixture add a little of a concentrated solution of any soluble sulphate and $BaSO_4$ precipitates. To another portion of the mixture add a little of a concentrated solution of any soluble barium salt and $BaSO_4$ precipitates. In the first case we increased the concentration of the SO_4'' until the solubility product was exceeded, in the second we increased the concentration of the $Ba^{\cdot\cdot}$ until the same thing occurred.

Make a saturated solution of $KClO_3$ and to it add a few drops of a concentrated solution of KCl. Some $KClO_3$ will precipitate, for this addition increased the concentration of the $K^{\cdot}$, and so caused the solubility product to be exceeded. To some more of the saturated solution of $KClO_3$ add a few drops of a concentrated solution of $NaClO_3$ and again $KClO_3$ precipitates. This time we increased the

concentration of the ClO_3' until the solubility product was exceeded. Instances of this sort might be multiplied almost indefinitely. We may extract a useful generalization from this. The solubility of a given salt is always diminished by the presence of a second salt with a common ion.

Formulation. We may formulate these principles as follows: Let m_0 = solubility of a binary electrolyte in water, expressed in gram-equivalent weights per liter. Let m = its solubility after the addition of the quantity x of a second binary electrolyte with a common ion. Let α_0 = the fraction of the original substance dissociated before the addition, and α = the fraction dissociated after the addition. Let α_1 = the fraction of the added substance dissociated. Then $m_0(1-\alpha_0)$ = quantity of original substance not dissociated before the addition, and $m(1-\alpha)$ = quantity of original substance not dissociated after the addition. In order that equilibrium shall be maintained between the excess solid and the dissolved but not dissociated substance, the quantity of the latter must remain the same, or $m_0(1-\alpha_0) = m(1-\alpha)$. In order that the other equilibrium between the undissociated substance and its ions shall be maintained the product of the ions must remain constant. The concentration of each ion before the addition is $m_0\alpha_0$ and the product is therefore $(m_0\alpha_0)^2$. After the addition the concentration of one ion is $m\alpha$ and that of the other is $m\alpha + x\alpha_1$. Therefore, $(m_0\alpha_0)^2 = m\alpha(m\alpha + x\alpha_1)$. Solving these equations for m we have:

$$m = m_0\frac{1-\alpha_0}{1-\alpha} \quad \text{and} \quad m = -\frac{x\alpha_1}{2\alpha} + \sqrt{m_0^2\frac{\alpha_0^2}{\alpha^2} + \frac{x^2\alpha_1^2}{4\alpha^2}}.$$

We can, then, calculate quantitatively what the solubility of a substance will be after the addition of a known quantity of a second electrolyte, from a knowledge of its solubility in pure water and of the degrees of dissociation. The latter may be determined by the conductivity method.*

Exceptions. There are cases where the facts do not correspond to the deductions from the solubility product. We cannot imagine that the fault lies with the premises of the law of mass action, nor in our method of formulating equilibria. We must therefore believe

* A. A. Noyes has proved that this formulation corresponds well with the facts in a number of cases. See, *Zeitschr. f. phys. Chem.*, **6**, 241–267 (1890), and *ibid*, **9**, 603–632 (1892). The application of the same principles to salts which upon dissociation give three ions is discussed by Noyes, *Zeitschr. f. phys. Chem.*, **26**, 152–158 (1898).

the cause of the divergence is to be found in our assumptions as to how dissociation takes place in these cases. The formation of complex ions for example upsets our calculations.

Complex Ions. If we add silver nitrate to a solution of $KClO_3$ we do not get a precipitate of AgCl. Chlorine is present, but is a part of the complex ion ClO_3' and the appearance of AgCl is evidently a test for the presence of Cl′, not for the element chlorine.

Add a solution of potassium thiocyanate to a solution of ferric chloride and we obtain a red color. Add it to a solution of potassium ferro- or ferricyanide and we get no red color. It is a test for the presence of the $Fe^{\cdots}$ and not for the element iron. The iron is present in the ferrocyanide as part of the complex ion, $Fe(CN)_6''''$, and in the ferricyanide as part of the complex $Fe(CN)_6'''$.

The addition of KNO_3 should lower the solubility of $Pb(NO_3)_2$ but the reverse effect is actually found. Noyes (*loc. cit.*) was able to account for this on the basis of the formation of complex ions. The subject is one of considerable importance in qualitative and quantitative analysis and should be taken up in detail in that connection.

Increasing the Solubility. The very same principles furnish a plausible explanation of the fact that some substances are more soluble in solutions of other substances than in pure water.

Add some NH_4OH to a solution of $MgCl_2$ and $Mg(OH)_2$ precipitates. Add a solution of NH_4Cl and this precipitate redissolves. The explanation is as follows: When the precipitation occurred the solubility product $C_{Mg^{\cdot\cdot}} \times C_{OH'}{}^2$ had been exceeded. The OH′ came from the relatively little dissociated NH_4OH. The addition of NH_4Cl, a much dissociated salt, greatly increased the concentration of the $NH_4^{\cdot}$. This drove back the dissociation of the NH_4OH. The formation of not dissociated NH_4OH removed OH′ from the solution until the product, $C_{Mg^{\cdot\cdot}} \times C_{OH'}{}^2$, was less than the solubility product of $Mg(OH)_2$, when, of course, the solid redissolved to reëstablish the equilibrium.

Add a solution of sodium tartrate to a solution of a calcium salt and calcium tartrate precipitates. Add a solution of tartaric acid to the same solution of a calcium salt and no precipitate results. The explanation is as follows: Sodium tartrate is strongly dissociated so that in a solution of this substance the concentration of the tartrate ion is large and this, multipled by the concentration of the calcium ion, exceeds the solubility product of calcium tartrate, which then precipitates. Tartaric acid is a weak acid, but slightly dissociated,

and thus a solution of this substance contains but a relatively small concentration of tartrate ion. This small concentration multiplied by the concentration of the calcium ion does not exceed the solubility product of calcium tartrate and therefore there is no precipitation.

Suppose we have a saturated solution of the difficultiy soluble salt, acid potassium tartrate, and add a strong, that is to say, a strongly dissociated acid. The hydrogen ions thus brought into the solution unite with tartrate ions to form undissociated tartaric acid. This diminishes the concentration of the tartrate ion and more acid potassium tartrate dissociates. The equilibrium thus destroyed reëstablishes itself only when more of the salt goes into solution.

According to our fundamental principles the solubility of aluminium hydroxide should be diminished in the presence of sodium hydroxide owing to the presence of the OH' common to both substances, but as a matter of fact aluminium hydroxide is soluble in an excess of either NaOH or KOH. The plausible explanation is that a complex ion forms in a way which may be represented by the reaction,

$$OH' + Al(OH)_3 = AlO(OH)_2' + H_2O.$$

Dissociation of Complex Ions. Silver cyanide dissolves in a solution of KCN and we have reasons to believe the solution contains $K^{\cdot}$ and the complex $Ag(CN)_2'$. This explains the fact that adding NaCl to the solution does not cause a precipitation of AgCl. But if we run H_2S into this solution we may get a precipitate of Ag_2S. We account for this by assuming that the complex ion is very slightly dissociated giving $Ag^{\cdot}$ and $2\,CN'$. The concentration of the $Ag^{\cdot}$ resulting from this dissociation is so small that the small solubility product of AgCl is not exceeded. But the solubility product of Ag_2S is yet smaller and is exceeded upon addition of H_2S.

Heterogeneous Chemical Equilibria between Solids and Gases. Ammonium chloride upon being heated vaporizes and dissociates in large measure to NH_3 and HCl. We have then a homogeneous equilibrium in the gaseous phase in contact with an excess of the solid. This amounts to a heterogeneous physical equilibrium superimposed on a homogeneous chemical equilibrium. Thus analyzed it is seen to consist of factors already considered. For the equilibrium between NH_3 and HCl on the one hand and gaseous but not dissociated NH_4Cl on the other, we may write $\frac{C_{NH_3} \times C_{HCl}}{C_{NH_4Cl\ gas}} = K_1$. For that between solid and gaseous, but not dissociated, NH_4Cl we

may write, $\frac{C_{NH_4Cl\ gas}}{C_{NH_4Cl\ solid}} = K_2$. As $C_{NH_4Cl\ solid}$ is a constant, the latter expression becomes, $C_{NH_4Cl\ gas} = K_3$. Then

$$\frac{C_{NH_3} \times C_{HCl}}{K_3} = K_1 \quad \text{or} \quad C_{NH_3} \times C_{HCl} = K_4.$$

Dissociation Pressure. The concentrations of gases are measured by their partial pressures and so, if p_1 is the partial pressure of NH_3 and p_2 the partial pressure of HCl, $p_1 p_2 = K_4$. This product of the partial pressures of the products of the dissociation is then a constant, called the dissociation pressure.

This product is in principle the same as the solubility product. We might call it a dissociation product. If we increase the concentration of either NH_3 or HCl the product is increased, the equilibrium is upset and solid must form. Diminish the concentration of either NH_3 or HCl and more solid must vaporize and dissociate.

If we add CaO to the system this combines with the HCl, diminishes the partial pressure of the latter, diminishes the " dissociation product " and more NH_4Cl must dissociate. In this way a large quantity of NH_3 must accumulate and so we see why an alkali " drives off " much NH_3 from an ammonium salt.

If we add phosphoric anhydride (P_2O_5) to the system, this unites with the NH_3 and a large excess of HCl gas is the logical and actual consequence.

NH_4HS vaporizes and dissociates to NH_3 and H_2S and the same reasoning applies without modification. Experimental investigations* have proved that the dissociation pressure does remain constant within the limits of experimental error, no matter how the concentrations of NH_3 and of H_2S are altered.

Solid ammonium carbamate, NH_4OCONH_2, vaporizes and dissociates to $2\,NH_3 + CO_2$. If C_1 is the concentration of the carbamate as a gas, C_2 the concentration of CO_2, and C_3 the concentration of NH_3, our general formulation gives the expression $\frac{C_2 C_3^2}{C_1} = K$, and the " dissociation product " contains the square of the concentration of NH_3. An increase in the concentration of the NH_3 must then throw back the dissociation much more than an equal increase in the concentration of the CO_2. This deduction too has been experimentally proven to be correct.†

* Isambert, *Compt. Rend.*, 102, 1313 (1886).

† Horstmann, *Liebig's Annal.*, 187, 48 (1877).

Upon heating calcium carbonate we obtain lime and carbon dioxide. $CaCO_3 \rightleftarrows CaO + CO_2$. Equilibrium is reached between these two solids and this gas when the concentration of the CO_2 has reached a definite value. This value is greater the higher the temperature, and is of course measured by its pressure. This pressure is called the dissociation pressure of calcium carbonate. Le Chatelier* investigated this case and following are some of the dissociation pressures which he determined, expressed in mm. of mercury.

547°	625°	740°	812°	865°
27	56	255	753	1333

At ordinary temperatures the dissociation pressure is so low that lime in contact with air takes up some of the carbon dioxide always present.

If, at any definite temperature, we compress the system and so increase the pressure of the CO_2 above the dissociation pressure for that temperature, CO_2 will unite with CaO to form $CaCO_3$ until the original pressure is reëstablished. If we continue to compress, endeavoring to maintain the higher pressure, the CO_2 will disappear entirely. Conversely, if we expand the system, more $CaCO_3$ will dissociate furnishing more CO_2 until the equilibrium pressure is reestablished. If we continue the expansion, endeavoring to maintain the lower pressure, all the $CaCO_3$ will vaporize and dissociate.

These are the experimental facts and they correspond well with the following deduction from our general formula. If C_1 is the concentration of $CaCO_3$, C_2 the concentration of CaO, and C_3 the concentration of CO_2, we may write $\frac{C_2C_3}{C_1} = K$. But the concentrations of solids are constants and so C_1 and C_2 may be included in K and we have $C_3 = K_1$. This tells us that for equilibrium at each temperature there is one, and only one, possible concentration of CO_2.

From this discussion we get the very practical hint that in "burning" limestone to make lime it hastens the process materially to blow a current of air or other indifferent gas over the limestone while it is being heated, to keep low the pressure of CO_2.

Looking at this system from the kinetic molecular standpoint one might at first think we could alter the equilibrium by adding more of one of the solids. For instance, one might think that adding CaO, some of the CO_2 present would unite with it to establish an

* *Compt. Rend.*, 102, 1243 (1886).

equilibrium in this freshly added mass, or that adding $CaCO_3$, a proportion of this addition would dissociate as did that originally present. It has been experimentally proved that neither of these things happens if the volume and pressure of the CO_2 is not altered. For each temperature there is one definite pressure (concentration) of CO_2 and we must make our theories fit these facts.

This is easily done. We assume that every solid has a vapor pressure though it may be so small we cannot measure it. Then we have solid $CaCO_3$ in equilibrium with gaseous $CaCO_3$ and solid CaO in equilibrium with gaseous CaO. The concentrations of these gases are entirely independent of the absolute quantities of the solids present, a general proposition carefully developed from experimental evidence in the chapter on vapor pressure. The chemical equilibrium may then be considered as establishing itself in the gaseous phase. The concentrations of two of the gases being held automatically constant by the presence of excess of the two solids, the concentration of the third must be fixed. This is the experimental fact we had to explain.

It would be well to follow this reasoning thoughtfully as it brings out the true significance of the statement that the concentration of a solid may always be treated as a constant in such formulations.

Water of Crystallization. If $CuSO_4.5\,H_2O$ is in a sealed tube containing no water vapor it will decompose according to the reaction $CuSO_4.5\,H_2O \rightleftarrows CuSO_4.3\,H_2O + 2H_2O$ until the water vapor has attained a definite pressure for a definite temperature. At 50° this pressure is 47 mm. and it is just like the other dissociation pressures we have been discussing. Add water vapor to the system, endeavoring to increase this pressure, and $CuSO_4.5\,H_2O$ will form. Remove water vapor and more $CuSO_4.5\,H_2O$ will decompose. As long as any of that phase remains we cannot permanently alter the pressure of the water vapor. If, however, we continue to remove water vapor until all $CuSO_4.5\,H_2O$ has gone, we can then lower the pressure gradually. But presently we come to another "sticking point," at a pressure of 29.8 mm. for 50°. Investigation will show that this is the vapor pressure (dissociation pressure) of $CuSO_4.3\,H_2O$ which dissociates similarly, according to the reaction: $CuSO_4.3\,H_2O \rightleftarrows CuSO_4.H_2O + 2\,H_2O$. Continuing to remove water vapor its pressure remains constant until all $CuSO_4.3\,H_2O$ has decomposed. Then first can we gradually lower the water-vapor pressure. As we do so we come to a third and last "sticking point," at 4.4 mm. at 50°. This is the dissociation pressure of $CuSO_4.H_2O$. It decomposes to maintain the constant

pressure as long as any remains. When it is all gone we have the anhydrous salt and may lower the water-vapor pressure gradually to zero.

The same principle applies to all salts with water of crystallization and determining the number of different definite water-vapor pressures obtained as we slowly dehydrate is a way to determine the number of salts with different amounts of water of crystallization which exist.*

Efflorescence. $CuSO_4.5\,H_2O$ does not ordinarily effloresce, because, as a rule, there is enough water vapor in the air to produce a pressure greater than its dissociation pressure. But sometimes it does effloresce and this means simply that the water-vapor pressure in the air is less than the dissociation pressure of the salt. This is the way to interpret all cases of efflorescence or absence of efflorescence.

Water Vapor, Hydrogen, and Iron. When water vapor is in contact with hot iron we may write the equilibrium,

$$3\,Fe + 4\,H_2O \rightleftarrows Fe_3O_4 + 4\,H_2.$$

Let C_1, C_2, C_3, and C_4 represent the concentrations of the substances in the order given and we may write $\frac{C_1C_2}{C_3C_4} = K$. C_1 and C_3 being concentrations of solids are constant and may be included in the equilibrium constant, and so we have $\frac{C_2}{C_4} = K_1$. This states that a constant ratio exists for any one temperature between the concentrations of the water vapor and the hydrogen. Remember that the partial pressure of a gas is a measure of its concentration. Let p_1 be the partial pressure of gaseous water and p_2 the partial pressure of hydrogen. Then $\frac{p_1}{p_2} = K_1$. The case has been carefully investigated by Sainte Claire Deville,† and by Preuner.‡ The latter investigator found experimental values of which those in the table on the next page, holding for 1150°, will serve as an example.

The constancy of the ratio is satisfactory and the deduction is in accord with the facts.

* For experimental methods and numerical values in other series of salts see W. Müller-Erzbach, *Zeitschr. f. phys. Chem.*, 19, 135–154 (1896).

† *Compt. Rend.*, 70, 1105, 1201; 71, 30 (1870).

‡ *Zeitschr. f. phys. Chem.*, 47, 385–417 (1904).

p_1	p_2	$\frac{p_1}{p_2}$
9.9	11.3	0.88
15.4	18.1	0.85
35.4	41.1	0.86
49.3	58.2	0.86

When we use this reaction to make hydrogen, we drive a lively current of steam over the iron. The concentration of the steam is then nearly constant and large. Hydrogen forms in an effort to raise its own concentration to the value indicated by the above ratio. But as fast as formed it is swept away by the current of steam. This factor of the equilibrium being thus removed, more hydrogen must form, and we can drive the reaction almost to completion.

If we send a rapid current of hydrogen over the hot oxide, the conditions are reversed while the reasoning remains the same. Water is formed in the effort to reach the conditions for equilibrium. But as fast as formed it is swept away by the current of hydrogen, so its concentration is kept low, and this reverse reaction can be forced to go practically to completion.

Conclusion. Individual instances of equilibrium might be multiplied until practically all the reactions known to the science of chemistry had been passed in review. But then this chapter would exceed all reasonable bounds. If the student understands the applications which have been made, he will surely be conversant enough with the principles, which really are simple and always the same, to formulate any other case whatsoever. As the imparting of this ability is the chief purpose of this chapter, we may consider this portion of the subject as finished and proceed to the next, which, important as it is, will require but little time.

Effect of Temperature on Equilibrium. As we have had occasion to remember over and over again, in determining equilibrium conditions the temperature must be specified and held constant. The question remains, How do equilibrium conditions alter when the temperature alters? We have as an answer that generalization not second in usefulness and wide applicability even to the law of mass action and the phase law, — the Le Chatelier-van't Hoff law of mobile equilibrium, first stated in Chapter XXIV. Let us restate it: When a system is in equilibrium, if we apply a force tending to alter a condition, the system will change in such a way as to minimize the alteration.

If we apply heat, tending to raise the temperature, the system will change in such a way as to absorb heat and minimize the temperature change. If a reaction, proceeding from right to left is exothermic, evolving a given quantity of heat, then proceeding from left to right it is endothermic, and absorbs exactly the same quantity of heat. Therefore, raising the temperature of a system in equilibrium will increase the concentration of an endothermic compound. We learn from this that to increase the yield of an endothermic compound we must operate at a higher temperature. The applications of this principle require a knowledge of the heats of formation and can therefore be treated more advantageously in the next chapter.

Catalysis and Equilibrium. The presence of a catalytic agent cannot possibly alter the conditions of equilibrium. This is easily and convincingly proved. Suppose a system normally reaches equilibrium conditions represented by E_1. Suppose the presence of a catalytic agent caused the system to reach equilibrium at different conditions represented by E_2. Insert the catalyser and produce the conditions E_2, then remove the catalyser, which of course remains unchanged in nature and amount. The system will then change from E_2 to E_1. Any process going of itself may be made to do work. We may then gain some work. Reinsert the catalyser and the system will go back to E_2. We might repeat as often as we pleased, gaining work at each repetition. In other words, we should have a perpetual-motion machine. But a perpetual-motion machine is impossible, therefore no catalytic agent can possibly alter the conditions of equilibrium.

It follows that a catalytic agent which increases the velocity of a given reaction must always and inevitably increase the velocity of the opposed reaction in the same measure.

CHAPTER XXVII

THERMOCHEMICAL DATA*

UNDER the head "thermochemistry" we classify all the facts and information we have obtained by studying changes of chemical energy into heat, and of heat into chemical energy. Since almost every chemical process either absorbs heat, in which case it is called endothermic, or evolves heat, in which case it is called exothermic, many "thermochemical" facts have already been considered, and we are once more reminded that our classifications are artificial and imperfect. Moreover, since the essential difference between different conditions of aggregation is the energy content, and this is always most conveniently measured in heat units, the last seven chapters may fairly be considered as devoted to special subdivisions of the large subject, "thermochemistry." There remain, however, many useful items of information still to consider.

Factors of Heat Energy. As has been said, temperature is the intensity factor of heat energy, and the quantity factor is measured in any one of several units. It may be well to review and summarize these.

Small Calorie. The small calorie, written cal., is the amount of heat required to raise one gram of water from 15° to 16°. It is necessary to state the exact interval because the specific heat of water varies with the temperature.

* Two authoritative works on thermochemistry are: "Thermochemische Untersuchungen," by J. Thomsen, in four volumes, published 1882 to 1886; and "Thermochimie, Données et Lois Numériques," by P. E. M. Berthelot, in two volumes, published in 1897.

J. Thomsen published an abridgment of his larger work, yet containing all his numerical results, and a translation of this appeared in 1908 under the title, "Thermochemistry," as one of the series of texts on physical chemistry edited by Sir W. Ramsay.

The most convenient place to find desired numerical results is in "Physikalisch-chemische Tabellen," Landolt, Börnstein, and Meyerhoffer, third edition, 1905, where the original reference is always given. The data used in this chapter were obtained from the last-named source except where other references are cited.

Large Calorie. The large calorie, written Cal., is the amount of heat required to raise 1000 grams of water from 15° to 16°.

Average Calorie. The average calorie, written K., is the amount of heat required to raise one gram of water from the temperature of melting ice to the temperature of water boiling under a pressure of 760 mm. It is then very nearly equal to 100 cal. or to 0.1 Cal.

Joule. The joule, written **j**, is based on the C. G. S. system of units, and so is the most scientific of all heat measures. But we must depend on the experimental determination of the mechanical equivalent of heat to determine the value of the joule, and new determinations may alter the present accepted value for the mechanical equivalent of heat. In such case, the unit for heat would have to be altered also, and this is a disadvantage. One joule is the quantity of heat equivalent to 10^7 ergs. This is sometimes inconveniently small, and therefore we multiply it by 1000 and obtain another unit, the Joule, written with a capital J, the quantity of heat equivalent to 10^{10} ergs, the symbol for which is J.*

British Thermal Unit. The British thermal unit, written B.T.U., is the amount of heat required to raise one pound of water one degree Fahrenheit.

Apparatus and General Methods. To obtain thermochemical data, we must measure the number of heat units evolved or absorbed when known quantities of substances react. In order that we may be able to make such measurements with a fair degree of accuracy, a reaction must go quickly and completely at ordinary temperatures. There are two large classes of processes which fulfill these conditions and about which we have fairly complete information. The first class comprises the processes of neutralization, of solution, and of dilution; the second, combustions. These latter often cause trouble by their too great rapidity, amounting at times to explosions.

Calorimeters in General. The apparatus used for measuring heat is called a calorimeter, and may have a great variety of forms, depending upon the particular process to be studied.

The main object sought in the construction of a calorimeter is the retention in it of all the heat produced. Loss of heat by conduction

* The mechanical equivalent of heat is, 1 cal. = 42 660 gram-cm. See Callendar and Barnes, *Phil. Trans.*, 199, 149 (1902). This, times 980.5 (gravity), gives ergs.

1 cal. = 4.183×10^7 ergs. Therefore, 1 cal. = 4.183 j and 1 j = 0.2391 cal.
1 cal. = 0.004 183 J and 1 J = 239.1 cal.

or by radiation brings a corresponding error into the measurements. So the vessel in which the reaction takes place is insulated as completely as possible from the surroundings by an envelope of some material which is a poor conductor of heat; for example, wool or feathers, or, best of all, a vacuum. To diminish loss or gain by radiation the outside is polished to a bright mirror-like surface if it is a metal and will admit of it. For the same reason glass vessels are often silvered.

Water Calorimeter. Excessive temperature changes are to be avoided because they make it more difficult to prevent losses of heat by radiation; so the calorimeter is generally arranged in such a way that the reaction warms a relatively large known quantity of water. An observation of the comparatively small change in temperature of this will give the necessary data for a calculation.

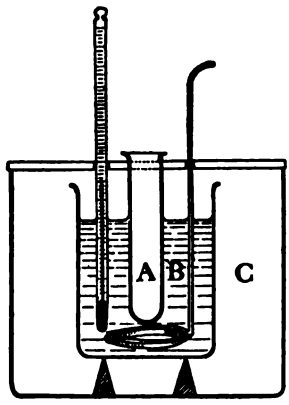


Fig. 63.

The essential features of such an instrument are indicated in Fig. 63. *A* represents a vessel in which the reaction is to be carried out. It is immersed in the water contained in *B*. *B* in turn is within a larger vessel, and the space *C* is packed with insulating material or often nothing is put in, as an air jacket insulates well enough for much work. A thermometer and a stirring device are inserted in the water in *B*.

Heat Capacity of Apparatus. We must determine the heat capacity of the whole apparatus. Suppose we put 300 grams of water at 22° in *A* when the water in *B* is at 19°, and suppose that after a short time the water in both *A* and *B* is found to be at 20°. This tells us that it takes 600 cal. to raise the temperature of the apparatus and water in *B* one degree. This is, then, the heat capacity. We may now remove the water from *A* and cause a reaction to take place in that vessel.

Determination of Heat of Neutralization. Suppose we wish to determine the heat of neutralization of a base with an acid, both in solution. One solution is put in the calorimeter and the other is in a vessel from which it may be transferred quickly to the calorimeter. Both solutions are brought as nearly as possible to the same temperature. The temperature is noted and they are mixed. After

time enough has elapsed for the reaction to be complete the temperature is noted again. Suppose the reaction raised the temperature three degrees. If the heat capacity of the apparatus is 600 cal., then three times 600 cals., or 1800 cals., which were evolved, went to raising the temperature of the apparatus. But to this we must add the number of calories required to raise the products of the reaction three degrees. We must know the specific heat of these products. If the reaction is between moderately dilute solutions, no serious error is introduced if we assume the specific heat to be that of water. A further calculation is necessary to convert these results into our system of chemical units, to determine how much heat is evolved when equivalent or molecular quantities interact. But this is sufficiently obvious not to require detailed description.*

Bomb Calorimeter. For reactions which go with explosive violence, we use a strong iron or steel vessel called a bomb calorimeter because it is sometimes shaped like a cannon shot or shell.† A known weight of the substance is put in and oxygen enough for complete combustion is run in under a pressure of about 20 atmospheres; or an excess of some substance which gives up oxygen readily, as do potassium chlorate or sodium peroxide, is mixed with the solid to be burned and the mixture is put in. The bomb is submerged in a known weight of water in an insulated vessel and the reaction is started by an electric spark or a wire heated electrically.

Ice Calorimeter. Bunsen's ice calorimeter is different in principle. The vessel in which the reaction is to take place is surrounded by another filled with dry ice at 0°. The heat evolved by the reaction melts a corresponding quantity of ice. The water thus formed is collected and weighed. Knowing the heat of fusion of ice, the calculation of the heat produced by the reaction follows at once.

Steam Calorimeter. Again, another calorimeter, particularly convenient in determining specific heats, is based upon the determination of the weight of water at 100°, which is condensed from steam at 100°, in raising the object through a known temperature interval.

Thermometers. It is important to measure the temperature accurately, and the thermometers made for thermochemical experiments

* For a description of a particularly carefully constructed calorimeter of this class, see T. W. Richards' "Energy Changes Involved in the Dilution of Zinc and Cadmium Amalgams." Publication No. 56 of the Carnegie Institution of Washington, 1906, pp. 52–54.

† The calorimetric bomb was invented and first used by P. E. M. Berthelot in 1884.

should be good, at least good enough to make readings to one-fiftieth of a degree. The Beckmann thermometer is a particularly useful instrument for such measurements.

Heat of Reaction. By heat of reaction we mean simply the number of heat units which are evolved or absorbed when reaction occurs between the formula-weight quantities in grams represented by the equation expressing the reaction.

Heat of Combustion. If the reaction represents a combustion, we speak of the heat of combustion, referring of course to the chemical unit quantity, the formula (or symbol) weight in grams. To be accurate, the product of the combustion should also be named, for the heat of combustion of carbon forming carbon monoxide is less than the heat of combustion of carbon forming carbon dioxide; the heat of combustion of sulphur to SO_2 is less than if the product is SO_3, etc.

Heat of Formation; of Neutralization. If the reaction represents the formation of a compound, we speak of the heat of formation; if the neutralization of an acid or base, we call it the heat of neutralization.

Heat of Solution, Dilution, Fusion, Vaporization. The significance of such phrases as "heat of solution," "heat of dilution," "heat of fusion," and "heat of vaporization" is self-evident, but it must be remembered that chemical unit quantities in grams are understood when we are studying chemistry.

The First Law of Thermochemistry. The first law of thermochemistry is an obvious and necessary corollary of the law of the conservation of energy. If the reaction takes place with the evolution of a given amount of heat, it absorbs precisely the same amount of heat when we, by any means, reverse it and obtain the original conditions again. This law was first stated by Lavoisier and Laplace in 1780, *i.e.*, sixty-one years before the law of the conservation of energy in its present comprehensive form.

Law of Constant Heat Summation. G. H. Hess (1802–1850), in 1840,* discovered and announced what we call the law of constant heat summation. The initial and final conditions alone determine the total heat effect of a reaction or series of successive reactions, and the intermediate steps may be few or many, but cannot alter this total heat effect.

* *Pogg. Annal.*, 50, 385 (1840). See also Ostwald's "Klassiker der exakten Wissenschaften," No. 9.

An Illustration of the Facts. The following table contains typical experimental results such as are summed up in the above statement. The final substance, $(NH_4)_2SO_4$, in solution, was made from H_2SO_4 and water and a dilute solution of ammonia by several different steps, the heat effect of each step being measured.

1.	$H_2SO_4 + 2\,NH_3$, Aq*		595.8
2.	$H_2SO_4 + H_2O$	77.8	
	$H_2SO_4H_2O + 2\,NH_3$, Aq	518.9	
	$518.9 + 77.8$	=	596.7
3.	$H_2SO_4 + 2\,H_2O$	116.7	
	$H_2SO_4\,2\,H_2O + 2\,NH_3$, Aq	480.5	
	$116.7 + 480.5$	=	597.2
4.	$H_2SO_4 + 5\,H_2O$	155.6	
	$H_2SO_4\,5\,H_2O + 2\,NH_3$, Aq	446.2	
	$155.6 + 446.2$	=	601.8†

The total heat effect is the same (within the limits of experimental error) whatever the intermediate steps.

An Application of the Law. This generalization is useful, as it enables us to calculate heats of reactions which cannot conveniently be determined experimentally. For example, we cannot measure the heat evolved when carbon burns to form carbon monoxide. But we can measure the heat evolved when the monoxide burns to form the dioxide, and also when carbon burns to form the dioxide. The results are expressed as follows:

$$C + 2\,O = CO_2 + 94\,300 \text{ cal.} \quad (1)$$

$$CO + O = CO_2 + 67\,700 \text{ cal.} \quad (2)$$

We may treat these symbols and formulæ as if they were algebraic symbols, and, subtracting equation (2) from equation (1), we obtain

$$C + O = CO + 26\,600 \text{ cal.} \quad (3)$$

Thus we find, with the aid of our generalization, what we could not otherwise determine, that the heat of combustion of carbon to the monoxide is 26 600 calories.

Energy Equations. The foregoing is an illustration of what is sometimes called an energy equation. The chemical symbols and

* It is customary to denote that a substance is in dilute solution by writing Aq after the formula.

† This example, original with Hess, may be found in the above form in Ostwald's "Lehrbuch der Allgemeinen Chemie," Vol. II, 1, p. 55.

formulæ are looked upon as standing for quantities of energy. We learn from equation (1) that the quantity of energy contained in the formula weight in grams of carbon dioxide is less, by a quantity of energy equivalent to 94 300 cal., than the sum of the quantities of energy contained in 12 grams of carbon and 32 grams of oxygen.

Must Regard the Conditions of Aggregation. When we consider the chemical symbols and formulæ as representing quantities of energy, it is necessary to differentiate with care between the conditions of aggregation, as a given weight of one and the same substance contains different quantities of energy as a solid, liquid, or gas.

Indicating Solids, Liquids, and Gases. In writing energy equations, it is customary to represent the solid condition of aggregation by printing the symbol or formula in heavy type, or by inclosing it within square brackets. The liquid condition of aggregation or solution is indicated by the use of common type, or by omission of parentheses. The gaseous condition of aggregation is indicated by printing in italics, or by inclosing the symbol or formula within curved parentheses.

For example: $H_2O = [H_2O] + 1440$ cal. means that a formula weight in grams of water when freezing liberates 1440 small calories. Again, $(H_2O) = H_2O + 10\,611$ cal. means that a formula weight in grams of water vapor in condensing liberates 10 611 cals.

Denoting Dilute Solutions. When a substance is dissolved in so much water that the addition of more, or the subtraction of a part of the water produces no heat effect, we denote it by writing Aq after the formula. Thus

$$NaCl,Aq + nH_2O = NaCl,Aq, \quad \text{or} \quad NaCl,Aq - nH_2O = NaCl,Aq.$$

Again,

$$KOH,Aq + HCl,Aq = KCl\,(Aq + Aq + H_2O) + 13\,750 \text{ cal.},$$

and the right-hand side of this equation simplifies at once to

$$KCl,Aq + 13\,750 \text{ cal.}$$

Illustration of the Use of Energy Equations. We may utilize energy equations to calculate heats of reaction which are not susceptible of direct measurement. We owe the following ingenious method of determining the heat of formation of sulphur trioxide to Hess.*

* *Pogg. Annal.*, 56, 463 (1842). Also, Ostwald's "Klassiker der exakten Wissenschaften," No. 9.

A mixture of lead oxide and sulphur is burned in oxygen and the heat evolved is measured. We find

$$[PbO] + [S] + 3\,(O) = [PbSO_4] + 1655\text{ K}. \qquad (1)$$

Lead oxide is next dissolved in dilute H_2SO_4, and this gives

$$[PbO] + H_2SO_4,\ 5\,H_2O = [PbSO_4] + 6\,H_2O + 233\text{ K}. \qquad (2)$$

Subtracting the second equation from the first, we get

$$[S] + 3\,(O) - H_2SO_4,\ 5\,H_2O = -\,6\,H_2O + 1422\text{ K},$$

or

$$[S] + 3\,(O) + 6\,H_2O = H_2SO_4,\ 5\,H_2O + 1422\text{ K}. \qquad (3)$$

That is, when sulphuric acid, in solution, is formed from sulphur, oxygen, and water, 1422 K are liberated. Sulphur trioxide is next dissolved in water and the heat is measured. This gives

$$[SO_3] + 6\,H_2O = H_2SO_4,\ 5\,H_2O + 411\text{ K}.$$

Subtracting this equation from equation (3), we get

$$[S] + 3\,(O) - [SO_3] = 1011\text{ K}, \quad \text{or} \quad [S] + 3\,(O) = [SO_3] + 1011\text{ K}.^*$$

By this calculation we have obtained the result desired, namely, the heat of formation of sulphur trioxide from sulphur and oxygen. Practically any heat of formation may be calculated in some such way, and it is a test of the ingenuity of the experimenter to choose suitable reactions; that is, reactions the heat of which may be readily measured, and yet which, by such combinations and algebraic processes, will quickly lead to the result.

Calculation of the Heats of Reaction by Means of Heats of Formation. In these energy equations we do not know the absolute amount of energy represented by our symbols and formulæ, for our thermochemical measurements are only of the quantities which change to heat. In order to have a definite starting point we put the energy of formation of the elements empirically as equal to zero. The heats of formation of exothermic compounds must then be subtracted from zero in order to obtain the quantities of energy represented by their formulæ. For instance, lead iodide is an exothermic compound. Its formation from the elements is accompanied by the evolution of 39.8 Cal.† Therefore, the formula PbI_2 stands for

* This illustration in the above form may be found in W. Ostwald's "Lehrbuch der Allgemeinen Chemie," Vol. II, 1, p. 123. Notice the heat unit used is the average calorie, K, first proposed by Ostwald.

† Notice the heat unit used is the large calorie.

-39.8 Cal. Then, in order to calculate the heat of any reaction, we may put, in place of the chemical formulæ, the respective heats of formation, with their signs changed, and solve the equation by ordinary algebra.

Illustration. For example, suppose that we wish to know the heat of the reaction $[MgCl_2] + 2\,[Na] = 2\,[NaCl] + [Mg] + X$, where X is the heat of the reaction.

The heat of formation of $[MgCl_2]$, from previous experiments, or from tables, we know to be 151.0 Cal., and that of [NaCl] is 97.9 Cal. Substituting these values with their signs reversed, we have

$$-151.0 + 0 = -(2 \times 97.9) + 0 + X.$$

Solving, we find $X = 44.8$ Cal. The heats of formation are thus useful values, as with them we may calculate the heat of any reaction.

The following table contains thermochemical data concerning some common substances, excerpted from the extensive tables in Landolt, Börnstein, and Meyerhoffer's compilation. This table will suffice to show how thermochemical results are best expressed, — as energy equations, — and contains heats of reaction, of combustion, and of formation. The significance of the brackets has been described. The heat values are all expressed in large calories.

$$[Li] + H_2O + Aq = LiOH,Aq + (H) + 48.97 \text{ Cal.}$$
$$[Li] + (O) + (H) = [LiOH] + 11.5 \text{ Cal.}$$
$$[Na] + H_2O + Aq = NaOH,Aq + (H) + 43.34 \text{ Cal.}$$
$$[Na] + (O) + (H) = [NaOH] + 102.7 \text{ Cal.}$$
$$[K] + H_2O + Aq = KOH,Aq + (H) + 41.9 \text{ Cal.}$$
$$[K] + (O) + (H) = [KOH] + 104.6 \text{ Cal.}$$
$$[K] + (Cl) + 3\,(O) = [KClO_3] + 93.8 \text{ Cal.}$$
$$[K] + (Cl) + 4\,(O) = [KClO_4] + 112.5 \text{ Cal.}$$
$$(N) + 3\,(H) = (NH_3) + 12.2 \text{ Cal.}$$
$$(N) + 5\,(H) + (O) + Aq = NH_4OH,Aq + 90.0 \text{ Cal.}$$
$$[Ca] + (O) = [CaO] + 145.0 \text{ Cal.}$$
$$[Mg] + (O) = [MgO] + 143.3 \text{ Cal.}$$
$$(H) + (Cl) = (HCl) + 22.0 \text{ Cal.}$$
$$(H) + (Cl) + Aq = HCl,Aq + 39.3 \text{ Cal.}$$
$$2\,(H) + (O) = H_2O + 68.43 \text{ Cal.}$$
$$2\,(H) + 2\,(O) + Aq = H_2O_2,Aq + 47.5 \text{ Cal.}$$
$$2\,(H) + [S] = (H_2S) + 2.7 \text{ Cal.}$$
$$[S]^* + 2\,(O) = (SO_2) + 69.26 \text{ Cal.}$$

* Rhombic sulphur.

$$[S] + 3\,(O) = [SO_3] + 103.7 \text{ Cal.}$$
$$[S] + 4\,(O) + 2\,(H) = H_2SO_4 + 192.2 \text{ Cal.}$$
$$(N) + 3\,(O) + (H) = HNO_3 + 41.5 \text{ Cal.}$$
$$[C] \text{ diamond} + (O) = (CO) + 26.1 \text{ Cal.}$$
$$[C] \text{ diamond} + 2\,(O) = (CO_2) + 94.3 \text{ Cal.}$$
$$[C] \text{ graphite} + 2\,(O) = (CO_2) + 94.8 \text{ Cal.}$$
$$[C] \text{ amorphous} + 2\,(O) = (CO_2) + 97.65 \text{ Cal.}$$

Allotropic Forms. The last three equations show that there is a heat effect when one form of carbon changes to another, and that one form contains more energy than another. We cannot measure this directly but we can calculate it. We see at once that a change of amorphous carbon into diamond must be accompanied by the evolution of 3.35 Cal., a change of diamond into graphite must be accompanied by the absorption of 0.5 Cal., etc.

The energy equation expressing the change of ozone into ordinary oxygen is $(O_3) = 1\frac{1}{2}\,(O_2) + 36.2$ Cal., which tells how much more energy ozone possesses than oxygen. This may be one reason for its greater chemical activity. [P] white = [P] red + 3.71 Cal. is a similar instance, the white variety containing more energy and being more active chemically than the red.

Heats of Formation of Carbon Monoxide and Dioxide. *A priori*, one would expect, if there is a difference in the amounts of heat evolved as successive atoms of oxygen unite with carbon, that combination with the first atom would evolve the more heat. This is, however, not the case. Combination with the first atom evolves 26.1 Cal., combination with the second evolves 68.2 Cal. It has been suggested in explanation of these facts that when the first addition takes place much heat goes into heat of liquefaction and heat of vaporization of carbon, for the product is a gas. The very practical conclusion from these particular thermochemical results is that, to get the maximum effect from a given quantity of coal, we must have plenty of oxygen, for if it burns to the first oxide only, we lose over two-thirds of its value.

Heats of Solution. The following few energy equations will serve to give a general idea of the thermochemical data upon the process of solution and dilution:

$$H_2SO_4 + H_2O = H_2SO_4,H_2O + 6.38 \text{ Cal.}$$
$$H_2SO_4 + 2\,H_2O = H_2SO_4,2\,H_2O + 9.42 \text{ Cal.}$$
$$H_2SO_4 + 9\,H_2O = H_2SO_4,9\,H_2O + 14.95 \text{ Cal.}$$

$$H_2SO_4 + 799\,H_2O = H_2SO_4,799\,H_2O + 17.6\text{ Cal.}$$
$$H_2SO_4 + 1599\,H_2O = H_2SO_4,1599\,H_2O + 17.9\text{ Cal.}$$
$$(HCl) + H_2O = HCl,H_2O + 5.37\text{ Cal.}$$
$$(HCl) + 2\,H_2O = HCl,2\,H_2O + 11.36\text{ Cal.}$$
$$(HCl) + 10\,H_2O = HCl,10\,H_2O + 16.16\text{ Cal.}$$
$$(HCl) + 50\,H_2O = HCl,50\,H_2O + 17.1\text{ Cal.}$$
$$(HCl) + 300\,H_2O = HCl,300\,H_2O + 17.3\text{ Cal.}$$

Question of Hydrates. Whether these, and other acids, which behave similarly, form hydrates with water cannot be determined from thermochemical data, because the heat effect gradually and continuously increases with the amount of water, slowly and more slowly approaching a maximum, without any abrupt change or " nick in the curve " which we might expect when we had the right proportions if a hydrate formed.

$$[NaOH] + 200\,H_2O = NaOH,200\,H_2O + 9.9\text{ Cal.}$$
$$[KOH] + 250\,H_2O = KOH,250\,H_2O + 13.3\text{ Cal.}$$
$$[CaO] + 2500\,H_2O = Ca(OH)_2\,2499\,H_2O + 18.3\text{ Cal.}$$
$$[NaCl] + 100\,H_2O = NaCl,100\,H_2O - 1.2\text{ Cal.}$$
$$[Na_2SO_4] + 100\,H_2O = Na_2SO_4,100\,H_2O + 0.4\text{ Cal.}$$
$$[Na_2SO_4.10\,H_2O] + 400\,H_2O = Na_2SO_4,410\,H_2O - 18.8\text{ Cal.}$$
$$[KBr] + 200\,H_2O = KBr,200\,H_2O - 5.1\text{ Cal.}$$
$$[KNO_3] + 200\,H_2O = KNO_3,200\,H_2O - 8.5\text{ Cal.}$$

The solution of neutral salts is, in most instances, an endothermic process. This is explainable on the hypothesis that a good deal of heat must be absorbed as heat of liquefaction and heat of vaporization before the solid solute can get into the dissolved state, which in so many ways resembles the gaseous condition of aggregation.

Organic Compounds. Organic compounds usually form so slowly and so incompletely that we cannot measure the heat of formation directly, but must use our indirect methods. Complete combustions in a bomb calorimeter give us the data for the following calculation of the heat of formation of methane.

$$(CH_4) + 2\,(O_2) = (CO_2) + 2\,H_2O + 213.5\text{ Cal.} \qquad (1)$$
$$[C]\text{ diamond} + (O_2) = (CO_2) + 94.3\text{ Cal.} \qquad (2)$$

Subtract (2) from (1) and obtain (3):

$$(CH_4) + (O_2) - [C] = 2\,H_2O + 119.2\text{ Cal.} \qquad (3)$$
$$2\,(H_2) + (O_2) = 2\,H_2O + 2 \times 68.4\text{ Cal.} \qquad (4)$$

Subtract (3) from (4) and obtain (5):

$$-(CH_4) + [C] + 2(H_2) = 17.6 \text{ Cal.} \qquad (5)$$

Transposing, we have, [C] diamond $+ 2(H_2) = (CH_4) + 17.6$ Cal., the heat of formation sought.

We may obtain the same result more simply by substituting heats of formation with the signs reversed in equation (1):

$$-x + 0 = -94.3 - 2 \times 68.4 + 213.5, \text{ and } x = 17.6.$$

Effect of a Change in Volume. When one formula quantity of a gas forms, it occupies a volume (at normal conditions) of 22.4 liters. In forming, it pushes back against the pressure of the surrounding gases and so does work. This work is done at the expense of internal energy, *i.e.*, of heat, and so the heat observed is less by the heat equivalent of that work. This heat equivalent is readily calculated as follows: Imagine a gas in a long cylinder closed by a piston whose area is one cm^2. Normal atmospheric pressure on that piston is 760 mm. of mercury or 1033.3 grams. If the expansion is one formula volume, the piston is pushed through 22 400 cm.; *i.e.*, $1033.3 \times 22\,400$ gram-cms. of work are done. 42 660 gram-cms. equal one small cal., therefore $\frac{1033.3 \times 22\,400}{42\,660}$ gives the calories equivalent to this volume change (= 542.3 cal. or 0.5423 Cal.).

This amount must then be added to the observed heat of reaction if the volume increases, and must be subtracted if the volume decreases by one chemical unit volume.

Correction is Independent of the Pressure. Notice that the actual pressure under which the volume change occurs makes no difference in this heat value because of the behavior of gases. If the pressure is doubled the volume of a gas is halved; that is, twice the weight, (2×1033.3), is pushed through half the distance, and so, of course, the work done remains the same.

Correction is Proportional to the Absolute Temperature. But the temperature at which the reaction occurs does make a difference. If the gas is evolved at $+273°$ it will occupy twice the volume it would at 0°, the conditions for which we calculated, and the same weight would be pushed back twice as far; *i.e.*, twice as much work would be done. If it could be evolved at the absolute zero, it would (theoretically) occupy no volume, and no work would be done. The correction is thus proportional to the absolute temperature.

We may say, then, that the correction is $\frac{542.3}{273} \times T = 1.986\ T$ small calories, where T is the absolute temperature at which the volume change occurs. For all ordinary purposes it is sufficiently accurate to say the correction is $2\ T$ small calories for each formula volume change.

Initial and Final Conditions Only Need be Considered. If the process is a combustion, the temperature may be high while the gas is being evolved, but this makes practically no difference. The generalization which we have called the law of constant heat summation tells us that the initial and final conditions determine the heat effect, independent of intermediate steps, few or many, and the final measurement is made at but slightly above the initial temperature.

A substance precipitating or going into solution involves heats of fusion and of vaporization, as has been said, and these complicate the problem very much.

Heat Effect. There is a convenient word in the German language, "Wärmetönung," for which we have no exact equivalent. We may translate it, "heat effect," but must define precisely what we mean by the term.* Let us denote by "heat effect" the algebraic sum of the heat quantities evolved or absorbed in a reaction, corrected for the work done by, or upon, the system through any volume change; the whole referred to the symbol and formula quantities expressed in the equation. It is the sum of the heats of formation of the molecules formed, diminished by the heats of formation of those which disappear, in the reaction, the whole corrected for change of volume if such change accompanies the reaction. It can evidently be either a plus or a minus quantity.

HEATS OF COMBUSTION AND OF FORMATION OF HOMOLOGOUS SERIES OF SATURATED HYDROCARBONS.

	Heat of combustion.	Difference.	Heat of formation.*
	Calories.	Calories.	Calories.
CH_4	213.5		17.6
		158.8	
C_2H_6	372.3		21.5
		156.1	
C_3H_8	528.4		38.1
		158.8	
C_4H_{10}	687.2		32.0

* These heats of formation are calculated from the heats of combustion according to the method just described, disregarding the correction for volume change. Verifying these values is good practice.

The constancy of the difference between successive heats of combustion is apparent; the addition of CH_2 increases the heat of combustion about 158 Cal.

HEATS OF COMBUSTION AND OF FORMATION OF THE ETHYLENE SERIES.*

	Heat of combustion.	Difference.	Heat of formation.
	Calories.	Calories.	Calories.
C_2H_4	341.1	158.2	−15.7
C_3H_6	499.3	150.9	−11.2
C_4H_8	650.2	153.8	+ 0.6
C_5H_{10}	804.0		+ 9.5

The first two members of the ethylene series are endothermic compounds, forming with the absorption of heat.

The addition of CH_2 appears to make the same constant difference in the heats of combustion of this series.

The series of alcohols and acids show the same regularity and about the same increase in the heats of conbustion for each addition of CH_2.

Heats of Organic Reactions. The heats of organic reactions are usually small and can seldom be measured directly, but must be calculated. For instance, the formation of ethyl ether from ethyl alcohol occurs according to the reaction: $2\,C_2H_5OH = (C_2H_5)_2O + H_2O + X$. Substituting the heats of formation with signs reversed, we have: $-2 \times 69.9 = -70.5 - 68.4 + X$, from which we find $X = -0.9$ Cal., a small value, according to which the reaction is endothermic.

Possible Errors. Such calculations are not of much value because of the probable error. The heat of formation of ethyl ether is calculated from the heat of combustion, and this has been found experimentally to be 651.7 Cal. Suppose an error of 1 per cent was made in this determination, and such an error is by no means unlikely in thermochemical work. This would amount to 6.5 Cal., and so, perhaps, the heat of formation of ethyl ether is 6.5 Cal. more than the value used in the above calculation. If so, X would equal +5.6 Cal., and the reaction would appear to be exothermic.

Thermoneutrality. Besides the law of constant heat summation, we owe two other interesting and important generalizations to Hess.

* These heats of formation also are calculated from the heats of combustion, disregarding the correction for volume change. For many similar tables illustrating other regularities see the authorities cited on p. 404.

The first is known as Hess's law of thermoneutrality, and the second is the statement that the heat effect in many neutralizations is a constant.*

If we mix dilute solutions of many pairs of salts, such as potassium nitrate and sodium chloride for instance, no heat is evolved nor absorbed. Hess's law of thermoneutrality has been expressed as follows: The double decomposition of neutral salts in dilute solution is accompanied by no heat effect.

Writing the metathesis between potassium nitrate and sodium chloride as an energy equation, we have

$$NaCl,Aq + KNO_3,Aq = KCl,Aq + NaNO_3,Aq + o\ Cal.$$

This reaction certainly looks as though something happened and we should expect heat to be either evolved or absorbed.

Dissociation Theory a Plausible Explanation. Hess could not account for the absence of heat effect, but our dissociation theory furnishes a plausible explanation. Let us rewrite the same reaction in the terms of the theory:

$$Na^{\cdot} + Cl' + K^{\cdot} + NO_3' = Na^{\cdot} + Cl' + K^{\cdot} + NO_3'.$$

From this it is evident that we have the same things on the two sides of the equality mark; that is, in spite of first appearances, nothing happens, and so, of course, there is no heat effect. This is an interesting illustration of the usefulness and wide applicability of the dissociation theory.

Exceptions to the Law also Plausibly Explained by the Dissociation Theory. Hess's law of thermoneutrality does not apply in all cases. The behavior of some salts, for instance those of cadmium or mercury, is not expressed by the law at all. But those solutions which we find do not correspond to Hess's law of thermoneutrality do not conduct electricity well either. They give osmotic pressures corresponding more nearly to normal molecular weights than to smaller molecular weights. In other words, all the experimental evidence conforms to the hypothesis that those solutes are not dissociated to any great extent. This being the case, we have no right to write the equation in terms of the ions; something *does* happen when their dilute solutions are mixed, and thus the exceptions themselves furnish additional evidence of the plausibility and usefulness of the theory of electrolytic dissociation.

* *Pogg. Annal.*, 50, 385 (1840). Reprinted in Ostwald's "Klassiker, der exakten Wissenschaften," No. 9.

Heat of Neutralization is a Constant. The second of these interesting generalizations is as follows: When a formula weight of a strong monobasic acid in dilute solution is neutralized by means of a strong alkali such as sodium or potassium hydroxide, likewise in dilute solution, the heat effect is always practically the same, no matter what the acid, and no matter what the base. The following are some such reactions written as energy equations:

$$HCl,Aq + NaOH,Aq = NaCl,Aq + 13.745 \text{ Cal.}$$
$$HNO_3,Aq + NaOH,Aq = NaNO_3,Aq + 13.68 \text{ Cal.}$$
$$HNO_3,Aq + KOH,Aq = KNO_3,Aq + 13.77 \text{ Cal.}$$

Plausible Explanation Furnished by the Dissociation Theory. At first it seems extraordinary that the same quantity of heat should be evolved no matter which one of these acids is neutralized by no matter which base; that the formation of sodium chloride, of sodium nitrate, or of potassium nitrate in dilute solution is always accompanied by the same evolution of heat. But if we rewrite these reactions in the light of the dissociation theory, they appear as follows:

$$H^{\cdot} + Cl' + Na^{\cdot} + OH' = Na^{\cdot} + Cl' + H_2O.$$
$$H^{\cdot} + NO_3' + K^{\cdot} + OH' = K^{\cdot} + NO_3' + H_2O.$$

Canceling or disregarding the ions which appear on both sides of the equality mark, for they have evidently undergone no change, all these equations become the same and represent the formation of undissociated water from its ions.

Heat of Formation of Water from Its Ions. Thus, according to the dissociation theory, the neutralization of a strong acid by a strong base in dilute solution consists solely in the formation of undissociated water from its ions, and this constant quantity, 13.7 Cal., is then in truth the heat of formation of undissociated water from its ions according to the reaction, or energy equation:

$$H^{\cdot} + OH' = H_2O + 13.7 \text{ Cal.}$$

Naturally, the heat of formation of water from its ions is an entirely different quantity from the heat of formation of water from its elements.

Heat of Dissociation. Exceptions to the above generalization are found when we use either a weak acid or a weak base in the neutralization. The weak acid or weak base is supposed to be incompletely dissociated, and it must dissociate and furnish hydrogen or hydroxide ions before these can unite to form undissociated water. The varia-

tion from 13.7 Cal. we attribute to the heat of this preliminary reaction, the dissociation of the undissociated substance. This gives us a method for determining the heat of dissociation, which may be either positive or negative. For instance, we find

$$NaOH,Aq + HF,Aq = NaF,Aq + 16.27 \text{ Cal.},$$

and we consider the difference, $16.27 - 13.7 = 2.6$ Cal., to be the heat evolved in the dissociation of HF.

In another instance we find

$$NaOH,Aq + HCN,Aq = NaCN,Aq + 2.9 \text{ Cal.}$$

Then $2.9 - 13.7 = -10.8$ is the heat of dissociation of hydrocyanic acid.*

The Principle of Maximum Work. Efforts to utilize thermochemical data to foretell whether or not a given reaction will take place, and in which direction, resulted in a statement called the "Principle of Maximum Work." This principle, which had its inception in the mind of Hess, was more explicitly formulated by Thomsen and received its most definite statement from Berthelot, was discussed briefly in Chapter VI. Berthelot stated it as follows: † "Every chemical process accomplished without the intervention of any external energy tends to produce that substance or system of substances which evolves the most heat."

Contradictions of the Principle. It is a close approximation to the truth in many cases, but there are many others which directly contradict it. According to this principle, no endothermic reaction could occur of itself, and yet we know of numerous endothermic reactions. For instance, acetylene forms from hydrogen and carbon at the temperature of the electric arc, and the energy equation for this synthesis is $2[C] + H_2) = (C_2H_2) - 51.4$ Cal. Many salts dis-

* Both HF and HCN are supposed to be partially dissociated in dilute solution and the heat differences as calculated above are only the heat effects of the dissociation of those portions not already dissociated. To each must be added the heat effect of dissociating that fraction of a formula weight which is already dissociated in dilute solution. Making these corrections, we have

Heat of dissociation of a formula quantity of HF $= +3.1$.
Heat of dissociation of a formula quantity of HCN $= -11.1$.

† "Tout changement chimique accompli sans l'intervention d'une énergie étrangère tend vers la production du corps ou du système de corps qui dégage le plus de chaleur," P. E. M. Berthelot. "Essai de Mécanique Chimique fondée sur la Thermochimie," Vol. II, p. 421 (1879).

solve in water with the absorption of heat. But the most important contradiction is the fact that many reactions (theoretically all reactions) proceed until they reach a condition of equilibrium, while, according to the principle, they should proceed to completion in the direction evolving most heat. The principle then denies the possibility of equilibria, and as equilibria certainly do exist, it is a statement contrary to fact and must be abandoned. Efforts to sustain it by explaining such "exceptions" on the basis of external energies are not entirely satisfactory.

Van't Hoff has explained the fact that the principle seems to apply in so many cases by calling attention to the fact that it surely would hold, rigorously, at the absolute zero; and our living conditions, around 290°, are not so very far removed from the absolute zero, relatively speaking.* Le Chatelier calls it an extremely interesting first approximation towards a strictly valid law.†

Le Chatelier's Law. Le Chatelier, endeavoring to modify and improve Berthelot's statement, was led to the generally applicable law which we discussed in Chapter XXIV and again in Chapter XXVI. It is hardly necessary to restate it.

Illustrated by the Oxides of Nitrogen. The standard illustration of Le Chatelier's law is the equilibrium $2\,NO_2 \rightleftarrows N_2O_4$. This reaction proceeds from left to right with the evolution of heat, and from right to left with the absorption of heat. A convenient way to show this qualitatively is as follows: Put some liquid N_2O_4 in three tubes 10 to 30 cm. long, sealed at one end. After enough has evaporated to displace the air, seal the other ends. At room temperature the contents will be distinctly brown, and we have equilibrium between the two substances. NO_2 is dark brown, while N_2O_4 is nearly colorless. Reserve one tube for comparison and heat the second. Its contents become much darker brown, showing that more NO_2 has formed; *i.e.*, that occurred which absorbed heat. Cool the third by immersing it in a freezing mixture, and its contents become much lighter brown, showing that more N_2O_4 has formed; *i.e.*, that occurred

* We estimate the temperature of the electric arc at the negative pole as 2500°; at the positive pole as 3900° (Rossetti). (Between 3000° and 4100° according to Le Chatelier.) The temperature of the sun is estimated at 9965° by Rossetti; at 7600° by Le Chatelier; at 5400° by Paschen. These values are calculated from the intensity of radiation, determined by the methods of optical pyrometry. See G. Bredig, "Ueber die Chemie der extremen Temperaturen," 1901.

† H. Le Chatelier "Leçons sur le Carbone, la Combustion, les Lois Chimique," p. 217 (1908).

which evolved heat. The dissociation may be followed quantitatively by vapor-density determinations at different temperatures.

Applied to Endothermic Reactions. According to the law endothermic processes are more likely to occur the higher the temperature. Hydrogen and oxygen unite with the evolution of more heat than is evolved by any other reaction known to chemistry (comparing equal weights), and yet at very high temperatures water dissociates measurably.*

Formation of Ozone. Another illustration is the formation of ozone when an electric discharge occurs through oxygen. That ozone may be formed at low temperatures when oxygen is passed between electrodes possessing high potential difference is but one of several phenomena indicating that the conditions we call high electric tension resemble in some way conditions of high temperature.

The Law Does not Enable Us to Foretell Chemical Occurrences. Le Chatelier's law is applicable to every instance of equilibrium, and, theoretically at least, every reaction reaches equilibrium if given time. But it leaves undecided the fundamental question whether or not a reaction will take place when two substances are brought together, and also the question as to what causes reactions to take place.

Conclusion. The data of thermochemistry give us measurements of chemical energy in terms of heat, but these are always measures of total energy, products of the intensity by the capacity factors, and they never give us a measure of one of the factors apart from the other. They are comparable to measurements of total electrical energy as products of amperes and volts.

Whether a reaction takes place or not depends exclusively on the intensity factor, and hence this study does not furnish us with any sure and universal rule to prognosticate chemical occurrences.

* The per cent dissociated at different temperatures was given on p. 173.

CHAPTER XXVIII

ELECTROCHEMISTRY — I *

THE QUANTITY FACTOR

UNDER the head of " electrochemistry " belong all those facts, generalizations, and theories which, together, comprise our knowledge regarding the processes in which electrical energy is converted to chemical energy or the converse.

Electrical energy is, of course, a better term than electricity. The latter noun suggests that there is something which we might isolate, weigh, and describe as we do sulphur or mercury, and which we should call electricity. Failing in this, many feel that electricity is peculiarly marvelous, a private province for wizards only. One, not in the least astonished that when one end of a poker is thrust in the fire, the other end gets hot, regards, with a species of awe, the fact that a wire will conduct electricity. By " marvelous " we should, apparently, understand "novel" or "unfamiliar," for there is nothing

* So comprehensive and important a subject as electrochemistry cannot be covered in two chapters. The effort has been made to present the principles of particular interest to chemists fully enough to be understood by beginners. For additional information the reader is referred to the following books.

Texts:

M. Le Blanc, "A Textbook of Electrochemistry," translated from the fourth German edition by W. R. Whitney and J. W. Brown, 332 pp. (1907).

R. A. Lehfeldt, "Electrochemistry," 268 pp. (1904).

R. Lüpke, "The Elements of Electrochemistry," translated by M. M. P. Muir, 223 pp. (1897).

Laboratory directions and numerical data:

F. Kohlrausch and L. Holborn, "Das Leitvermögen der Elektrolyte," 211 pp. (1898).

Ostwald-Luther-Drucker, "Physiko-Chemischer Messungen," third edition, 573 pp. (1910).

Alexander Findlay, "Practical Physical Chemistry," 282 pp. (1906).

Frederick H. Getman, "Laboratory Exercises in Physical Chemistry," 241 pp. (1904).

And also the standard authorities, Ostwald, Nernst, and the "Tabellen" of Landolt, Börnstein, and Meyerhoffer.

intrinsically more marvelous in electrical phenomena than there is in the attraction of gravitation, and that a weight will fall to the ground if dropped. The most familiar incident of everyday life, such as the dissolving of a lump of sugar in a cup of tea, is marvelous if we mean, as we usually do by that word, that we cannot understand how it happens.

It will not be amiss to restate the "point of view" which it is one of the main purposes of this book to inculcate, and to remind the reader that all our knowledge of properties and processes (*i.e.*, substances and energies) consists solely of descriptions which are inevitably incomplete. We know most about that energy which we can most readily and accurately measure, and the modes of behavior of which we can most successfully formulate. Judged by this criterion we know as much about electrical energy (electricity) as about any other form, and more than we do about most other forms.

Efforts to attribute to electrical energy weighable and volume-occupying properties seem to be more numerous and more insistent than like efforts regarding any other form of energy. The phlogiston theory of heat was converted to a curio by Lavoisier at the end of the eighteenth century. "Clerk-Maxwell may be credited with the remark that Faraday's work had the result of banishing the term 'the electric fluid' into the limbo of newspaper science," * by the middle of the nineteenth century, and yet the term "current" probably implies a lingering belief in an objective, weighable, flowing liquid.

The idea that there are two kinds of "electricity," positive, denoted by a plus sign, and negative, denoted by a minus sign, is still more firmly established, and has crystallized into the language until it is, at the present time, in vain to endeavor to avoid using it. Such conventions are justifiable if they facilitate expression, if only it can be remembered that they are conventions like our symbols, lines, and the pictographs containing both, with which we indicate the architectural features of molecules. Insidious as these devices are, they are indispensable.

The electron theory is gradually altering these conventions and substituting improvements; but these are still conventions. The present fashion is to speak somewhat as follows: There is only one kind of "electricity," and that is of the minus variety. A univalent anion in solution is whatever the symbol or formula stands

* See "Michael Faraday," by Sylvanus P. Thompson, p. 218.

for, plus an electron; a univalent cation is whatever the symbol or formula stands for, less an electron. Bivalency is supposed to correspond to the presence of two extra electrons or the absence of two which were originally present, and so on. There are distinct advantages in this method of representing facts; it is a plausible and useful theory, one we should know. The familiar disadvantage attaches to it, though, for there is an undeniable inclination on the part of some to accept it too eagerly, somewhat with the feeling, " at last we know what electricity is." This finds expression in what is called " the atomic structure of electricity," as if anybody knew anything about " atomic structure." We do not know what " electricity " really is any more than we know what heat, light, chemical energy, or any other form of energy " really is." But we can measure it and formulate its manifestations.

As with other forms, we simplify our problems if we divide the total electrical energy into a capacity factor and an intensity factor, in such a way that the product of these factors equals the total energy, and establish units for the measurement of each factor separately. Although the fundamental units in which we express these factors, and the instruments used in measuring them, are doubtless well known to the majority of my readers, a brief summary follows:

The Galvanometer. The galvanometer is the instrument most used to detect and measure an electrical current. It consists, in its simplest form, of a magnetic needle suspended within, or close to, a coil of wire. In working with this instrument it is convenient to remember Ampere's rule.

Ampere's Rule. Suppose a man swimming in the wire in the direction of what we call the " plus current " and with his face toward the needle. Then the north-seeking end of the needle will be deflected toward his left hand. In a galvanometer of the d'Arsonval type, a " horseshoe " magnet is in a fixed position and a small coil of wire is suspended between its poles. When a current is passed through this coil it turns, and from the deflection the quantity of electrical energy which is passing per unit time may be calculated. Such an instrument, provided with a pointer and scale, is called an amperemeter, sometimes an ammeter, from the name of our unit of current quantity.

Resistance. Between the two ends of a constant source of electrical energy, such as a cell of a storage battery, place a copper wire of uniform cross section and known length, and also an ampere-

meter, and note the quantity of the current. Then substitute double the length of wire and it will be found that the current quantity is halved. The wire then conducts electrical energy, but offers a certain resistance to its passage, and we furthermore learn from many such experiments that the quantity of current is inversely proportional to the resistance. Next double the source by connecting two cells in series; *i.e.*, connect the plus terminal of the first to the minus terminal of the second, and connect the original wire and amperemeter to the minus terminal of the first and the plus terminal of the second. (Of course if all these signs are reversed the result is the same.) Twice the quantity of current will now flow through the amperemeter. We have doubled the driving force, the electromotive force, the intensity factor of electrical energy (commonly written e.m.f.), and find that by so doing we have doubled the current quantity. From many such experiments we have learned that the quantity of current is directly proportional to the electromotive force.

Ohm's Law. Combining these generalizations, we have what is known as Ohm's law, first announced by a German physicist, G. S. Ohm (1781–1854), in 1827. Let C = quantity of current, E = electromotive force, and R = resistance, then $C = \frac{E}{R}$, the fundamental formulation of the relationship between the units.

Ohm. The unit of resistance is called the ohm. Owing to the difficulty in making absolute measurements, based on the C. G. S. units, the international, legal ohm is defined as the resistance of a thread of mercury 106.3 cm. long and one mm.^{2} in cross section, at 0°. This quantity of mercury weighs 14.4521 g. This particular length was selected in order that the electrical units as a whole should stand in a simple relationship to the C. G. S. system. Another unit, formerly much used, now little used, is the mercury, or Siemens unit. It is the resistance of a thread of mercury as above, but just one meter long. Ohm is often indicated by the symbol ω.

Coulomb. The unit for the quantity factor of electrical energy is called the coulomb, in honor of the French engineer and physicist, C. A. Coulomb (1736–1806). Again because of the difficulty of making absolute measurements, it is defined as the quantity of electrical energy which will deposit 1.118 mg. of silver. Time does not enter into this definition, but it does into the following.

Ampere. The unit of current quantity is called the ampere, from the French physicist and chemist, A. M. Ampere (1775–1836). A

current of one ampere delivers one coulomb per second. One one-thousandth part of an ampere is a milliampere, a unit much used in laboratory investigations.

Volt. The unit for the intensity factor of chemical energy, the electromotive force, is called the volt, so named in honor of Count A. Volta. (1745–1827), an Italian physicist, and is derived from the other two units, the ohm and the ampere, using Ohm's law. One volt is the intensity, or electromotive force, which will cause a one-ampere current to pass through one ohm.

Joule. Total electrical energy is of course the product of the intensity factor by the quantity factor. The unit is called the Joule, so named in honor of J. P. Joule (1818–1889), an English physicist. Coulombs × volts = Joules. Here again the time element does not enter; but it does into the following.

Watt. The technical unit in which electrical energy is measured is called the watt, from James Watt (1736–1819), the Scotch inventor. It is the power to do work of a current of one ampere with an intensity of one volt. In buying and selling electrical energy the unit is the watt-hour; *i.e.*, what a one-volt one-ampere current delivers in one hour. The kilowatt is, of course, one thousand times this. For instance, an incandescent lamp is called a 40-watt lamp if, when the voltage is 100, 0.4 ampere passes through the filament, or if, when the voltage is 200, 0.2 ampere passes through the filament, and so on. Suppose an electric lighting company charges 12 cents per kilowatt; hours is understood, and so, to run this lamp, it will cost $\frac{40}{1000} \times 12 = 0.48$ cent per hour.*

Methods of Measurement. The methods of making the most common measurements may be understood from Fig. 64. *A* and *B* are the terminals of a storage battery, the source of a constant supply of electrical energy. *C* is an amperemeter, an instrument constructed with a short coil of large wire through which the whole of the current passes. *R* is a resistance box containing spools of insulated wire, each spool having a known resistance, as 1 ohm, 2 ohms, 5 ohms, etc. The resistances in such a box are usually related to each other as

* One ohm is intended to equal 10^9 C. G. S. units. One coulomb is intended to equal 10^{-1} C. G. S. units. One volt is intended to equal 10^8 C. G. S. units. The best absolute measurements we have give: One ohm is nearly 1.0002×10^9 C. G. S. units; one coulomb is nearly 0.9998×10^{-1} C. G. S. units. It follows that one volt is practically what it was intended to be: One joule = coulombs × volts = 10^7 C. G. S. units. For further discussion of these units see texts on physics.

weights in a box of weights. The ends of the wires are soldered to brass blocks adjacent to, but not touching, each other. By inserting or removing brass plugs these blocks may be connected, or the connection may be broken in such a way that the current must pass through the attached spool. In this way the total resistance of the box may be varied at will. Such an instrument is often called a rheostat. Suppose we have removed plugs and counting up find R equals 120 ohms; suppose all connections are made with stout wires, such that the resistance of the circuit outside the rheostat is negligible as compared with that in the box; suppose the amperemeter shows 0.05 ampere passing. Since $C = \frac{E}{R}$, we have $0.05 = \frac{E}{120}$ or $E = 6.0$ volts.

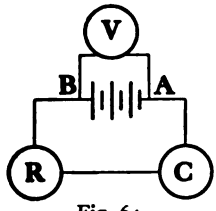


Fig. 64.

V is a voltmeter, an instrument made like an amperemeter but containing a coil of very long fine wire, *i.e.*, with a high internal resistance. If it is used to determine the voltage of a battery, it is connected directly to the two terminals as shown. It is said to be inserted as a "shunt," the term used to indicate that it affords another and independent path for the current. As its resistance is so high, only a small part of the current passes through it. It should be noted, however, that a small portion does pass through it and must pass through it; otherwise it would give no reading. This error is not negligible in exact measurements. Suppose we do not know the value of R, but that the voltmeter shows 10 volts and the amperemeter 0.2 ampere. We have, then, $0.2 = \frac{10}{R}$, or $R = 50$ ohms. Finally, suppose we have no amperemeter, but the voltmeter reads 8 volts and we have 40 ohms out of R. Then $C = \frac{8}{40}$, and 0.2 ampere must be passing through the circuit.

"Fall in Potential." Suppose we have a long wire with a total resistance of 2 ohms and apply an e.m.f. of 2 volts at the ends. Attach a voltmeter to one end and the middle; it will read one volt. This illustrates the fact that Ohm's law, $C = \frac{E}{R}$, applies to any part of the circuit as well as to the whole circuit. We say the "fall in potential" along half the wire is one volt, the "fall in potential" along the whole wire is 2 volts. It is plain that the fall in potential

between any two points in any circuit is the same fraction of the whole e.m.f. applied at the ends as the resistance included between the points is of the whole resistance.

Calculating the Current in a Branching Circuit. In Fig. 65 a current passes through an amperemeter C and then at A forks, part passing through resistance R_1, part passing through resistance R_2, to come together again at B. Suppose the amperemeter reads 0.5 ampere and that we know $R_1 = 2$ ohms and $R_2 = 8$ ohms.

Fig. 65.

We wish to know how many amperes pass through each branch. Conductance is the name given to the property, ability to conduct; and, as the word implies, it is the reciprocal of the resistance. The greater the resistance, the less the conductance, and vice versa. Branch R_1, having a resistance of 2 ohms, may be said to have a conductance of $\frac{1}{2}$, and by the same reasoning branch R_2 may be said to have a conductance of $\frac{1}{8}$. Now the conductance of R_1 plus the conductance of R_2 provides for the passage of all that passes, or 0.5 ampere, and the quantity passing through each branch is directly proportional to its conductance. Then the quantity passing through R_1 (x) is to the quantity passing through R_2 (y) as $\frac{1}{2}$ is to $\frac{1}{8}$, or $\frac{x}{8} = \frac{y}{2}$, or $x = 4y$. Furthermore, the sum of these two parts is the whole current, or $x + y = 0.5$ ampere. Thus we find $y = 0.1$ ampere and $x = 0.4$ ampere.

Wheatstone Bridge. One of the most used combinations of instruments is known as the Wheatstone bridge, from Sir Charles Wheatstone (1802–1875), an English physicist and inventor. In Fig. 66 a current forks at A, part going through resistance R_1 and R_2 to the point of recombination at B, part going through R_3 and R_4 to the same point B. A galvanometer, G, is connected in such a way as to form a bridge from a point between R_1 and R_2 and a point between R_3 and R_4. Now if R_1 is to R_2 as R_3 is to R_4, no current will cross this bridge, but if this exact proportion does not exist, some current will pass through the galvanometer. Suppose R_4 is a wire whose resistance we wish to determine. We adjust the other three resistances until there is no deflection, and knowing these can at once calculate the fourth, for $R_1 : R_2 = R_3 : R_4$, and so $R_4 = \frac{R_2 R_3}{R_1}$.

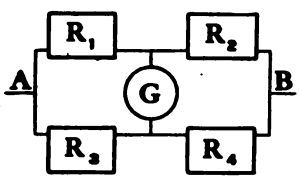


Fig. 66.

In determining the resistance of electrolytes we utilize this principle with the modifications shown in Fig. 67. *A* represents a battery, the current from which is led to a small induction coil *I*, which preferably vibrates rapidly, giving out a high note, familiar as that

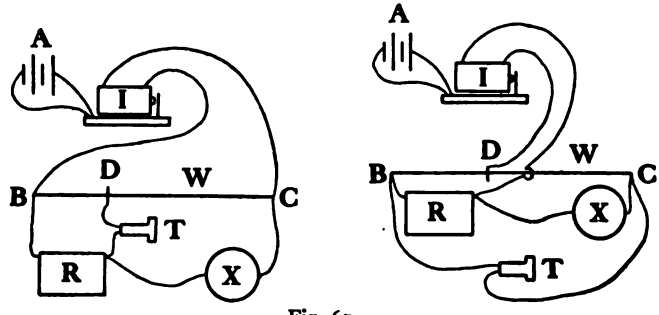


Fig. 67.

of a mosquito. The secondary alternating current is sent through a wire *BC*, of high resistance, stretched along a meter stick or wound on a drum which can be revolved.

The current forks at *B*, part passing along the wire, part passing through the rheostat *R* and the cell *X* containing the electrolyte, and the two parts unite again at *C*. *D* is a knife-edge arranged in such a way that it may be slid along the wire. From a point between *R* and *X* a wire leads to the telephone *T*, and the other wire from the telephone leads to the knife *D*. We thus have a Wheatstone bridge in which the portion of the wire *BD* corresponds to R_1 of Fig. 66, the portion of the wire *DC* corresponds to R_2, *R* corresponds to R_3, and *X* to R_4. When the resistance of *BD* is to the resistance of *DC* as the resistance of *R* is to the resistance of *X*, no current will pass through the telephone. When an alternating current passes through a telephone, a loud buzzing noise is heard; if no current passes, of course the telephone is silent. If the wire is uniform, the resistance of the two parts are to each other as their lengths, and as all we require for our calculation is the ratio, we do not need to know the resistance of the wire. For instance, suppose in making a measurement we have the resistance of $R = 110$ ohms and have moved the knife till the telephone is silent, and then find *D* is 350 mm. from *B*. We then have, $350 : 650 = 110 : X$, from which we calculate at once that $X = 204+$ ohms.*

* Wires are seldom if ever so uniform that we can use the lengths directly without introducing too great an error. Such a wire must be calibrated. This

The other diagram in the same figure illustrates an alternative method of connecting the instruments. The wires from the coil and from the telephone have just changed places. The main advantage in this arrangement is that it gives a high e.m.f. where the knife touches the wire, and this is desirable, as this is the most uncertain contact in the whole arrangement.

Conductors and Nonconductors. Substances are classified as conductors and nonconductors, or insulators. Here, as with so many other properties of substances, there is no sharp line of demarcation but one merges into the other.

Classification of Conductors. Conductors may be divided into two classes. Conductors of the first class experience only heating effects from the passage of the current; metals and carbon belong to this class. The conductors of the second class suffer chemical change simultaneously with the passage of the current; this change is called electrolysis. Salts, either fused or in solution, acids and bases in solution, belong in this class. We call these solutions electrolytes.

When a current passes through an electrolyte, the metals are separated where the " positive electricity " leaves the solution, and the acid radicals are separated where the " negative electricity " leaves the solution. We may say, then, that the metals, and the replaceable hydrogen of acids, move with the positive current, while acid radicals and the hydroxyl group move with the negative current.

We call these portions of an electrolyte, which so move, the ions. The ions traveling with the positive current we call cations, and they separate out on the cathode. Those traveling with the negative current we call anions, and these separate out at the anode.*

Remembering the above conventions, it is easy to trace the direction of the current through any system of batteries and cells, however

is quickly and easily done as follows: Set up a Wheatstone bridge as indicated in Fig. 67, substituting a second rheostat R_2 for the cell X. Make $R = 10$ ohms and $R_2 = 90$ ohms. Find the position of the knife for silence in the telephone. Whatever this reading, it represents the point at which one-tenth of the total resistance of the wire is between B and D and nine-tenths is between D and C. Next make $R = 20$ ohms and $R_2 = 80$ ohms. The knife reading now will be the point at which two-tenths of the total resistance is between B and D. Next make $R = 30$ and $R_2 = 70$, and find the knife reading, and so on. The wire may readily be calibrated in this way at any desired intervals; the only thing to remember is that $R + R_2$ must always equal a constant number of ohms.

* Anion, by derivation, signifies that which goes up; cation signifies that which goes down.

varied. For instance, suppose we have a battery consisting of zinc and carbon plates, and that we are using it to copperplate something in a copper sulphate solution. The zinc is dissolving, that is, moving away from the zinc pole in the battery. Therefore, the plus current is doing likewise and comes out through the carbon plate, which is, on this account, frequently called the " plus " or " positive " pole or terminal. It passes on into the electrolytic cell and through this, taking the metallic copper with it and depositing this copper on the electrode connected with the zinc pole.

Faraday's Law. Suppose we have a number of cells, each provided with a pair of electrodes and connected in series, that is, one after the other in such a way that the current must pass through number one, then through number two, and so on. Thus, if the current is allowed to pass for a definite time, the same quantity of electrical energy will pass through each cell. Suppose the first cell contains acidulated water, the second a solution of silver nitrate, the third a solution of copper sulphate, the fourth a solution of a stannous salt, the fifth a solution of a stannic salt. If we interrupt the current when just 8 grams of oxygen have separated at the anode of number one, we shall find that 1.008 grams of hydrogen have separated at the cathode of that same cell; that 107.88 grams of silver have separated at the cathode of number two, and reactions have occurred at the anode of that same cell corresponding to the liberation of a formula weight of the ion NO_3' (either solution of the metal of the anode or decomposition of water with the liberation of 8 grams of oxygen); that 31.8 grams of copper have deposited on the cathode of number three, while reactions corresponding to one half the formula weight of the ion SO_4'' have occurred at the anode of that cell; that 59.5 grams of tin have deposited on the cathode of cell number four, and 29.75 grams of tin have deposited on the cathode of cell number five. Now all these quantities are chemically equivalent to each other; that is, they are each and all quantities with which unit quantity of chemical energy is associated. (It may be desirable for the reader to refer back to the chapter on chemical energy, affinity, and valence, wherein the concept of the quantity factor of chemical energy was developed at length.) This experiment has been carried out with a great many different substances, always with the same result; a given quantity of electrical energy always separates chemically equivalent quantities at the electrodes. This fundamental generalization, true for all instances of electrolysis, is known as

Faraday's law, from Michael Faraday (1791–1867), the English chemist and physicist who discovered it and announced it in 1833. The fact that we can make this generalization demonstrates that there is a very close relationship between electrical and chemical energies.

The Faraday. By definition, when 1.118 mg. of silver have been deposited one coulomb of electrical energy has passed, so when a symbol weight in grams (107.88) of silver has been deposited, $\frac{107.88}{0.001\,118} = 96\,493 +$ coulombs have passed. Our experimental methods are not accurate enough to justify us in considering this value correct to the last significant figure, and so it is customary to call it 96 500. This quantity of electrical energy, which is just sufficient in electrolysis to separate out a quantity of any substance, element or compound, which has associated with it unit quantity of ability to combine chemically, is often called a faraday. This quantity is comparable in its usefulness in all problems involving electrolysis with the usefulness of the quantity 22.4 liters in problems involving changes from weight to volumes of gases.

Coulometers. Faraday's law furnishes us with an almost bewildering choice of methods for determining the quantity of electrical energy which has passed through a circuit. We have only to insert an electrolytic cell in the circuit, at the close of the experiment determine by analytical methods the quantity of chemical change, and calculate from this directly the quantity of electrical energy which has passed. Such cells are generally called voltameters, but this is a misnomer, as they tell us nothing about volts, nor about amperes either, unless we simultaneously measure the time and are sure the current has not varied during the experiment. They do tell us, and some with a high degree of accuracy, the number of coulombs which have passed, and therefore they should be called coulombmeters, better abbreviated to coulometers.

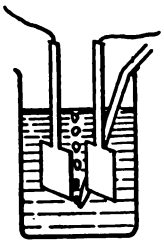


Fig. 68.

In a beaker containing a suitable electrolyte place an anode and a cathode as shown in Fig. 68. Having weighed the cathode, insert this arrangement in the circuit. At the close of the experiment, wash, dry, and weigh the cathode once more. The increase in weight is the weight of metal deposited, and from a knowledge of the weight in grams of the metal which has associated with it unit quantity of chemical energy, what is ordinarily known as the equivalent

weight of that metal, applying Faraday's law, we calculate at once the number of coulombs which have passed. For instance, we find one gram of silver has deposited; we know that 107.88 grams are deposited by 96 500 coulombs; therefore $\frac{1}{107.88} \times 96\,500 = 894.5$ coulombs have passed. Suppose we find that 1.5 grams of copper have deposited from a cupric sulphate solution; we know that 31.8 grams are deposited by 96 500 coulombs; therefore $\frac{1.5}{31.8} \times 96\,500 = 4552$ coulombs have passed.

A vast amount of work has been done perfecting details so that no loss shall occur mechanically or chemically. The silver coulometer particularly has been brought to a high degree of perfection because it has been made the legal ultimate standard of measurement of quantity of electrical energy. Fig. 69 shows a silver coulometer as recommended by Richards.*

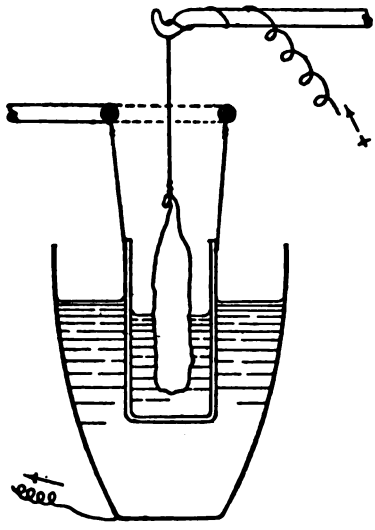


Fig. 69.

The cathode is a platinum crucible, and the anode a piece of pure silver suspended in a porous cup which catches any particles of silver which might become detached. The electrolyte, which should stand at a somewhat higher level outside than inside the porous cup, contains from 20 to 40 parts by weight of pure silver nitrate to 100 parts by weight of distilled water. For accurate results, it is not safe to allow more than 0.1 gram silver per cm.^{2} to deposit on the cathode. The current density must not exceed 0.2 ampere at the anode nor 0.02 ampere at the cathode.

Current Density. By current density we mean the quantity in amperes per unit area of electrode submerged in the electrolyte. If the total current passing is one ampere and the area of the anode is 5 cm.^{2}, the current density at the anode is 0.2 ampere. If the cathode

* T. W. Richards, E. Collins, and G. W. Heimrod, *Proc. Am. Acad. of Arts and Sciences*, 35, 123–150 (1899).

in the same cell has an area of 50 cm.², the current density at the cathode is 0.02 ampere. With this silver coulometer, it is possible to attain an accuracy of ± 0.03 per cent.*

The copper coulometer is not so reliable, but is amply good enough for many purposes. One form consists of copper electrodes in an electrolyte containing 150 g. copper sulphate, 500 g. sulphuric acid, 50 g. alcohol and 1000 g. water. The current density should not be below 2 nor above 20 milliamperes per cm.² of cathode. It is desirable to bubble a slow stream of carbon dioxide through the solution to keep it stirred.

A number of coulometers are based on the principle of measuring the volume of a gas evolved. For instance, water is electrolyzed and the hydrogen alone or the hydrogen and oxygen together are collected and measured and the simple calculation follows.

A convenient coulometer for measuring large quantities of current is illustrated in Fig. 70. The lower chamber of the apparatus contains two platinum electrodes, connected by heavy platinum wires sealed through the glass, submerged in 10 per cent to 20 per cent sodium hydroxide solution. The upper chamber contains calcium chloride between glass-wool plugs. This catches moisture while the hydrogen and oxygen escape. The whole apparatus is weighed before and after the experiment and the loss in weight is the weight of water electrolyzed. 96 500 coulombs electrolyze 9.008 grams of water. In case heavy currents are passed for a long time, it may be necessary to cool the cell.

Fig. 70.

Other coulometers, particularly for small quantities, are based upon the principle of determining by titration, for instance, the quantity of silver which has gone into a solution, or the quantity of iodine which has been separated from potassium iodide.†

* For full working directions see the original article (*loc. cit.*), or Ostwald-Luther-Drucker, "Physiko-Chemische Messungen," p. 496.

† See Ostwald-Luther-Drucker, "Physiko-Chemische Messungen," for details.

There are many applications of electrolytic processes, in technical and in analytical chemistry, of great interest and value, but it is not possible to include these, and the reader is referred to the standard works mentioned at the beginning of this chapter for information upon these topics. We shall now proceed to consider certain reasonings from the facts summarized in Faraday's law. These facts are most plausibly explained by Arrhenius's theory of electrolytic dissociation, which was first presented in Chapter XVI. This theory is not the only one possible, but it is so much the most useful we have as yet devised that it is the only theory with which we need to be thoroughly conversant.

It will be remembered that, according to this theory, any substance which in water solution conducts electrical energy is to be imagined as dissociating immediately upon solution, and independent of the presence or absence of electrodes or a current of electrical energy, into cations carrying "plus" charges, and anions carrying "minus" charges. We suppose that these ions actually transport the electrical energy somewhat as hod carriers transport bricks. A cation, arriving at the cathode, dumps its load of electrical energy there, and, becoming a different substance, acts otherwise than it acted as an ion. For instance, in a solution of KCl, we have potassium ions, $K^{\cdot}$, a compound of the element potassium and electrical energy in fixed and definite proportions, 96 500 coulombs of electrical energy and 39.10 grams of potassium. This compound is decomposed at the cathode, the electrical energy goes off through the wire and leaves free potassium, which then of course promptly decomposes water with the evolution of hydrogen and the formation of KOH, which equally promptly dissociates to $K^{\cdot}$ and OH'. It may be seen at once that in order to obtain a plausible explanation of Faraday's law we must assume that the copper ion carries two units charge. That is, 63.57 grams of copper, as ions, have associated with them $2 \times 96\ 500$ coulombs; for that is the amount of electrical energy obtained when enough of the compound, $Cu^{\cdot\cdot}$, is decomposed to give 63.57 grams of metallic copper. By the same reasoning, the stannous ion must consist of a symbol weight of tin united with two unit quantities of electrical energy, and is to be represented by $Sn^{\cdot\cdot}$, and the stannic ion must consist of a symbol weight of tin united with four unit quantities of electrical energy, and is to be represented by $Sn^{\cdot\cdot\cdot\cdot}$.

Solutions of sugar, alcohol, glycerol, etc., do not conduct electrical

energy (or the conduction is so small that it is negligible), so these solutions are not electrolytes, and we reason that there are no ions present, that these substances do not dissociate. Solutions of acids, bases, and salts do conduct, and we reason that there must be ions present. Moreover, the better they conduct, the more ions must be present, and so a measure of ability to conduct is a measure of the degree of dissociation.

The Conductivity Method. The experimental method which we use to determine the degree of dissociation on this principle was devised by F. Kohlrausch, and the arrangement of the measuring instruments has been described and illustrated in Fig. 67. The cells holding the electrolyte may be of various forms, adapted, each, to some special purpose. The most generally useful are small glass cylinders 3 or 4 cm. in diameter and 7 or 8 cm. deep, containing horizontal platinum disks as electrodes. The two forms most used are shown in Fig. 71. Stout platinum wires holding the electrodes are sealed into glass tubes, and these are sealed into hard rubber cell covers which fit the cell fairly well. This is in order that the electrodes may be removed and replaced in very nearly the same position. The glass tubes are filled with mercury, and wires dipping into this establish the necessary connections. It is not always easy to obtain silence in the telephone, and in almost all cases we must employ a sort of vibration method, moving the knife along the wire to the right to a definite small intensity of sound, and then to the left to a position of about the same intensity. The arithmetical mean between these two positions is taken as the reading. It has been found that, in most cases, coating the electrodes with platinum black by electrolyzing a solution of $PtCl_4$, occasionally reversing the direction of the current, makes it easier to determine the position of minimum sound in the telephone. The alternating current must be used in determining the resistance of the electrolyte, for a direct current would result in polarization, and no constant readings could be obtained. The resistance of an electrolyte varies with the temperature, in general falling off about 2 per cent for each degree increase in temperature, and

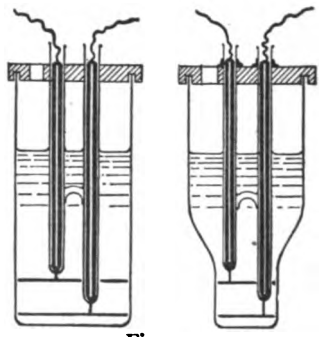


Fig. 71.

so the temperature must be known accurately and must be held constant. Therefore the cell is placed in a thermostat maintained at $25° \pm 0.1°$. This is the standard temperature adopted for these measurements. If another is used the fact is stated.

In this way we determine the resistance in ohms of the electrolyte between the electrodes in our cell, but this result cannot be used directly for comparing with results obtained with other electrodes in other cells. It must be calculated over to a standard.

Specific Resistance or Resistivity. From the measurement of the resistance in ohms of a copper wire of known length and diameter, we can determine what we call its specific resistance, or, as recent books call it, the resistivity. We now speak of the resistance of a definite wire of copper, but of the resistivity of the substance copper. The resistivity or specific resistance of a substance is the resistance in ohms of a centimeter cube of the substance between two parallel faces. The resistance of a wire is directly proportional to its length and inversely proportional to its cross section. If R = resistance in ohms, l = length in cm., q = cross section in cm.^{2}, and σ = resistivity, we have $R = \sigma \frac{l}{q}$, from which we may calculate resistivity from a measurement of length, cross section, and resistance, or may calculate the resistance of a given wire if we know the resistivity of the substance. For instance, by experiment we find that a hard copper wire, 500 cm. long with cross section of 1 mm.^{2} at 0°, has a resistance of $\frac{1}{12}$ of an ohm. Then $\frac{1}{12} = \sigma \frac{500}{\frac{1}{100}}$, or $\sigma = \frac{1}{600\,000}$. Again, knowing the resistivity of copper to be $\frac{1}{600\,000}$, we wish to know the resistance of a wire 5 mm.^{2} in cross section and one kilometer long. We have $R = \frac{1}{600\,000} \frac{100\,000}{\frac{5}{100}}$, or $R = 3.33+$ ohms.

Specific Conductance or Conductivity. As has been said, the reciprocal of the resistance is the conductance, and similarly, the reciprocal of the specific resistance or resistivity is the specific conductance or conductivity. This is commonly denoted by the Greek letter χ, and so $\chi = \frac{1}{\sigma}$. From the above figures, we see that the conductivity of hard copper at 0° is 600 000; or, as it is more usually expressed, 60×10^4. If L = conductance $\left(\frac{1}{R}\right)$ we have $L = \chi \frac{q}{l}$.

Our cells are almost never of dimensions to give the conductivity directly. We may measure the area of our electrodes and their distance apart, and, if they fit closely to the sides of the cell, may calculate at once. For instance, suppose the area of each electrode is 4 cm.^{2} and that they are just 1 cm. apart, and that we find the resistance is $\frac{1}{2}$ ohm. We have $\frac{1}{2} = \sigma \frac{1}{4}$, or $\sigma = 2$, and $\chi = \frac{1}{2}$.

Capacity Factor of a Cell. But the electrodes do not fit the sides closely, and so our "wire" is not of uniform cross section; the electrodes are not apt to be exactly parallel and the accurate measurement of their areas and distance apart is no easy task. We get around these difficulties as follows: We put in our cell an electrolyte whose conductivity is known and measure the resistance. The conductivity of an $\frac{n}{10}$ KCl solution at 25° is 0.012 89. Suppose our cell, containing this solution, gives us a resistance of 20 ohms. Then the conductance $L = \frac{1}{20}$. Inserting in the formula, we have $\frac{1}{20} = 0.012\,89 \frac{q}{l}$, or $\frac{q}{l} = \frac{1}{0.2578} = 3.879$. We have not found the distance between our electrodes nor their area, but this ratio is all we need. Suppose we put another electrolyte of unknown conductivity in that same cell and find $R = 50\omega$. We have only to substitute in the formula and obtain $\frac{1}{50} = \chi\, 3.879$, or $\chi = 0.005\,156$, the conductivity sought. It is more convenient to transpose and write the formula $\frac{1}{R} \frac{l}{q} = \chi$, and thus the reciprocal of our value for $\frac{q}{l}$, or $\frac{1}{3.879}$, or 0.2578, is evidently the number by which to multiply the conductance as measured in our cell to obtain the conductivity of the electrolyte within it. It remains a constant for that cell so long as the electrodes are not bent nor altered, but it is desirable to redetermine it at rather frequent intervals. It is called the capacity factor of the cell. Let us denote it by C; then $LC = \chi$. In words, the conductance times the capacity factor of the cell gives the conductivity.

Molecular Conductivity. Suppose we have a cell whose electrodes are just one centimeter apart and as large as we like. Between these electrodes let us put so much of the solution that one molecular weight in grams of the solute is present. The conductance of this cell so filled is the molecular conductivity of the substance. The molecular conductivity is denoted by μ. If we have a normal solu-

tion, *i.e.*, one containing a gram molecular weight in a liter, our electrodes must each have a surface of 1000 square centimeters, since there are 1000 cubic centimeters in a liter. If our solution is $\frac{1}{100}$ normal, we must have 100 liters between our electrodes in order to measure directly the molecular conductivity, and this would require electrodes with areas of 100 000 cm.^{2} or 10 square meters each.

Such enormous cells as would be required for the direct measurement of molecular conductivities are entirely impossible, but this is no drawback, for the values are so readily calculated. We find, in the way which has been described, the conductivity of a solution, and this, by definition, is the conductance of a centimeter cube. We then multiply this by the number of cubic centimeters which we should have to take in order to get one molecular weight in grams of the solute between the electrodes. For a normal solution we multiply by 1000; for a $\frac{1}{100}$ normal solution we multiply by 100 000. This volume, by which we must multiply the conductivity to obtain the molecular conductivity, is called the dilution and is denoted by V. Thus $\chi V = \mu_v$ or $LCV = \mu_v$.

Molecular Conductivity Varies. Suppose we have a liter of a normal solution of potassium chloride in our imaginary cell, and that we measure its molecular conductivity. Call this μ_{v_1}. If now we add pure water, we increase the dilution, but do not increase the amount of potassium chloride present. We find the conductivity, χ, of this more dilute solution is less, but when we multiply by the new dilution, V_2, we find the new molecular conductivity, $\chi V_2 = \mu_{v_2}$, larger than μ_{v_1}. The only plausible explanation for this fact is the assumption that by diluting we have increased the number of ions. These additional ions must have come from the dissociation of previously undissociated molecules of the solute, for the conductivity of pure water is so small it may be neglected.

"Infinite" Dilution. We may add more water, and find μ_{v_3} larger than μ_{v_2}, and again μ_{v_4} larger than μ_{v_3}, and so on until at last we reach a point where further additions of water do not increase the molecular conductivity any more. If we reach this maximum of molecular conductivity upon the tenth addition of pure water and then make an eleventh and twelfth addition, we shall find $\mu_{v_{10}} = \mu_{v_{11}} = \mu_{v_{12}}$, etc.

The plausible explanation of these facts is the assumption that with

the successive additions of water, more and more molecules of KCl have been dissociated to the ions $K^{\cdot}$ and Cl' until at last, all the molecules of KCl having been dissociated, further additions of water cannot bring more $K^{\cdot}$ and Cl' ions into existence. At this point dissociation is complete; the molecular conductivity is a maximum and constant.

It is usual to denote the molecular conductivity when dissociation is complete by the symbol μ_∞. This is often called infinite dilution, but by this term we do not mean an infinite amount of water, but an amount so large that more produces no further effect on the molecular conductivity.

Equivalent Conductivity. We determine the equivalent conductivity of a substance exactly as we determine its molecular conductivity, only using an equivalent weight in grams instead of a molecular weight in grams. It is customary to denote equivalent conductivity by λ and by λ_v. Thus λ_{10000} means the conductance of an equivalent weight in grams dissolved in 10 liters and between electrodes one centimeter apart. The dilution, V, is often expressed in liters instead of cubic centimeters, but no confusion is apt to result from this.

Following is a table showing the equivalent conductivities of some solutions at 25°. Dilution, V, is expressed in liters.

Dilutions	32	64	128	256	512	1024
KCl	135.7	139.4	142.4	145.7	148.0	149.1
NaCl	113.6	116.9	119.8	121.4	124.9	126.3
$\frac{1}{2}$ $MgCl_2$	108.2	113.5	118.0	121.6	124.6	127.4
$\frac{1}{2}$ $NiSO_4$	66.7	77.4	88.2	98.9	109.3	117.4
$\frac{1}{2}$ $Cu(NO_3)_2$	105.2	111.2	116.1	119.2	120.4	122.5
HCl	393	399	401	403	.....	.....
HBr	398	402	405	405	406	405*

* For many more similar tables see any of the larger works on electrochemistry, and particularly "Leitvermögen der Elektrolyte," by Kohlrausch and Holborn.

This table shows how equivalent conductivities increase with the dilution. In the case of HBr, the maximum is reached at the comparatively small dilution of 128 liters; it is reached for all practical purposes by all strong acids and salts of strong acids with strong bases, at or below a dilution of 2000 liters. In these measurements particularly pure water must be used, else its conductivity is not negligible. Distilled water good enough for analytical purposes is not nearly good enough for this. It must be distilled with special

precautions. Such water is usually referred to as "conductivity" water.*

The Degree of Dissociation. If a solution does not conduct at all we assume no ions are present; if a solution shows a maximum molecular conductivity, μ_∞, we assume that dissociation is complete. It follows that there is a direct proportionality between the conductivity and the number of ions, or degree of dissociation. This ratio, the fraction dissociated, is usually denoted by α. If μ_v is less than the maximum, then $\alpha = \frac{\mu_v}{\mu_\infty}$. In order to calculate α, μ_∞ must be known, and this may be determined by direct experiment in many cases, but in many others it is calculated by a method which has been developed from facts, and by reasoning, which we shall now consider.

The Rate of Migration of Ions. In a series of articles which appeared from 1853 to 1859, long before our present dissociation theory was advanced, W. Hittorf† described experimental methods and results, and suggested plausible hypotheses, not favorably received at the time, but now considered as fundamental, regarding the mechanism of conduction by electrolytes. He sent known quantities of electrical energy through electrolytic cells, determined the changes in concentration of the electrolyte about one or both electrodes, and from these analytical results determined the relative rates at which different ions transport the current.

Imagine we have a trough-like cell as represented in Fig. 72 filled with an electrolyte, say $\frac{n}{20}AgNO_3$ solution, and imagine it divided into an anode compartment A, a middle compartment B, and a cathode compartment C. Suppose we send a small current through this cell carefully, so that no gas is evolved, and so that all the current passes from the anode to the solution by the dissolving of silver, and all the current passes from the solution to the cathode by the depositing of silver. Then a definite quantity of silver will have been added to the solution in the anode compartment, and the same quantity of silver will have been taken out of the cathode compartment. Hittorf's apparatus was so devised that he could remove the contents

* See laboratory manuals for methods of preparing "conductivity" water. See also p. 460 for more details about the conductivity of water.

† *Pogg. Annal.*, **89**, 177–211 (1853); **98**, 1–33 (1856); **103**, 1–56 (1858); **106**, 337–411 and 513–586 (1859). These articles have been reprinted in Ostwald's "Klassiker der Exakten Wissenschaften," No. 21 and No. 23.

of the three compartments separately and analyze them. He found that the concentration of silver nitrate was increased in the anode compartment, but not enough to correspond to all the silver dissolved, and was decreased in the cathode compartment, but not enough to correspond to all the silver deposited, and that it remained unchanged in the middle compartment. This is what one would expect, since silver dissolves from the anode and is deposited on the cathode; but there is more to the phenomenon. The change in concentration observed is not solely a change in the quantity of silver; each compartment contains neutral $AgNO_3$ after, as before, the experiment, and so NO_3' ions must have left the cathode compartment and have traveled to the anode compartment, while $Ag^{\cdot}$ ions traveled in the opposite direction. The way in which we can, from these concentration changes, calculate the relative rates at which $Ag^{\cdot}$ ions and NO_3' ions transport electrical energy is ingenious.

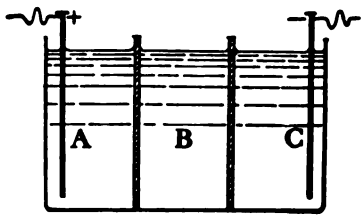


Fig. 72.

The quantity of current which passes any definite point in a circuit in a given time is the same as that which passes any other point in the circuit in the same time; this is a fundamental and self-evident fact regarding conduction. At the point of contact between our anode and solution, it is all carried by + ions going into solution; at the point of contact between solution and cathode, it is all carried by + ions going out of solution. How is it carried past a point represented by a cross section within the solution? We believe it is carried by ions, and that we have both + and − ions engaged in the process. Let us confine ourselves for the sake of simplicity to univalent ions such as we have here in our illustration, $Ag^{\cdot}$ and NO_3'. If 10 $Ag^{\cdot}$ ions move across our boundary from left to right, a definite quantity of electricity will have passed that point; if 10 NO_3' ions move across our boundary from right to left, the same quantity of electricity will have passed that point, and in the same direction; if 5 $Ag^{\cdot}$ ions cross from left to right and 5 NO_3' ions cross from right to left, we shall have the same result again; and lastly, if 4 $Ag^{\cdot}$ ions cross from left to right and 6 NO_3' ions cross from right to left, we once more have the same result. The total current transference is the quantity transferred by the cations plus the quantity

transferred by the anions. The fraction of the whole carried by one kind of ion is what is known as the transference number for that ion.

Now let us refer back to our cell. We must conduct our experiment in such a way that the concentration in the middle compartment is not changed, otherwise our analyses of the contents of the anode and cathode compartments will not give us the true values of the concentration changes produced by the current. We must, therefore, use a small current for not too long a time, say 10 milliamperes for 2 hours. From these results we can, by simple multiplication, calculate the changes which would have arisen if we had sent unit quantity, 96 500 coulombs, through the cell. Suppose the anode and cathode compartments are so large they each contain an equivalent weight (107.88 grams) silver, as ions, to begin with. Suppose that by solution of the anode another equivalent weight of silver has been added. If none left this compartment, we should find two equivalent weights of silver there at the end. But we do not; we find, and this is the result of actual experiment, 1.527 equivalent weights of $Ag^{\cdot}$ ions and the same, *i.e.*, 1.527 equivalent weights, of NO_3' ions. It is clear, then, that 1 − 0.527 or 0.473 equivalent weights of silver have moved out of this compartment, and that 0.527 equivalent weights of NO_3' ions have moved into it. The "door" of this compartment is a cross section in the solution, and we now have a good picture of how the current passes through this door. We may say 0.473 of the current is carried by + ions ($Ag^{\cdot}$ ions) crossing from left to right, while 0.527 of the current is carried by − ions (NO_3' ions) crossing from right to left. As each ion carries the same quantity of electrical energy, it follows that when 473 $Ag^{\cdot}$ ions have crossed to the right, 527 NO_3' ions have crossed to the left, and so the velocity of migration of the cations $Ag^{\cdot}$ is to the velocity of migration of the anions NO_3' as 0.473 is to 0.527. These are the quantities we have called the transference numbers.

A word of caution is needed here. It might appear to be a necessary result of such a mechanism that an excess of negative ions shall accumulate to the left, and an excess of positive ions to the right, of any such imaginary boundary. This does not happen; experiments prove the solution remains neutral at all points. It could not happen because of the heavy charges on the ions which cause them to attract each other. It must be remembered that positive ions are constantly being added at the anode and removed at the cathode, evi-

dently at just the rate requisite to maintain the neutrality. Fig. 73 is an effort to illustrate graphically how we imagine these concentration changes come about. + signs represent cations and − signs anions. The double row at *a* represents the even distribution to begin with. If the conduction consisted solely in 10 cations going into the solution at the anode, passing evenly through the solution and pushing, so to speak, 10 cations out of the solution at the cathode, while the anions took no part in the current transference, the picture

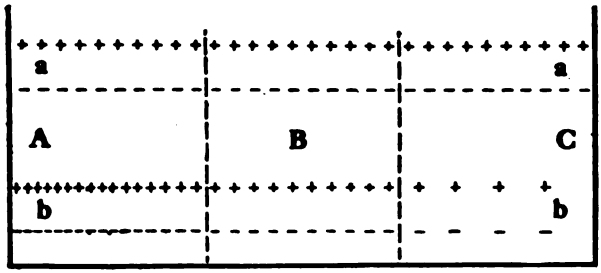


Fig. 73.

would not be altered. But now let us express graphically what we believe occurs (only assuming the transference numbers are cation 0.4 and anion 0.6, as we have no convenient way to picture the actual fractions). Ten cations have entered compartment *A*, while 4 have left. Then 16 are there, more or less crowded up near the electrode, but spread to an even distribution in *B*. Ten cations have left compartment *C* and only 4 have entered it, so they are thinly spread near the electrode. Six anions have left compartment *C*, the same number are in *B* as originally there, and 6 anions have entered compartment *A*. Thus for each cation there is an anion, and the double row *b* pictures the experimental results and shows how the anions can move 6 units of distance to the left, while the cations move but 4 to the right, without disturbing the neutrality of any part of the solution.

The loss in the anode compartment is 4, while that in the cathode compartment is 6, and these are the transference numbers we assumed in this demonstration. We may then formulate as follows:

$$\frac{\text{loss in anode compartment}}{\text{loss in cathode compartment}} = \frac{\text{velocity of cation}}{\text{velocity of anion}}.$$

But it will also be noticed that a determination of the change in concentration around one electrode is all that is necessary to calculate

the transference numbers of both ions. One form of apparatus at present used in the laboratory is shown in Fig. 74.* The right leg of the *H*-shaped vessel is filled to a level indicated by *a–a* with a concentrated solution of copper nitrate in which is a copper cathode. The apparatus is filled to the level indicated by *bbbb*, with $\frac{n}{20}$ $AgNO_3$ solution, and a silver anode is near the bottom of the left leg. The connections with the electrodes are protected by glass tubes. In one experiment careful analysis showed that the solution, to begin with, contained 0.007 39 gram $AgNO_3$ per gram of water. A small current was sent through for two hours. A silver coulometer was in series with the experiment, and 0.0780 gram silver was deposited on its cathode. This amount is 0.000 723 of an equivalent weight in grams of silver (Ag = 107.88). After the circuit was broken, the solution about the anode was taken out through the stopcock and analyzed. It contained 23.14 grams water and 0.2361 gram $AgNO_3$. This much solution before the passage of the current contained $23.14 \times 0.007\,39 = 0.1710$ gram $AgNO_3$. The amount of $AgNO_3$ in the anode compartment had then increased by $0.2361 - 0.1710 = 0.0651$ gram. This increase is 0.000 383 of an equivalent weight in grams of silver and also the same fraction of an equivalent weight in grams of nitrate ion. The quantity of silver which dissolved from the anode must have been the same as that which deposited on the cathode of the coulometer, as that was the only way in which electrical energy passed that point of the circuit. (If any gas had evolved, the experiment would have been worthless for the calculation in hand.) Since 0.000 723 equivalent weight of silver was added and the increase found was 0.000 383, the difference, or $0.000\,723 - 0.000\,383 = 0.000\,340$, is the amount which migrated out of the anode compartment. While this was going on, 0.000 383 equivalent weight of NO_3' migrated into the compartment. Thus the velocity of migration of the $Ag^{\cdot}$ is to the velocity of migration of the NO_3', as 0.000 340 is to 0.000 383. The

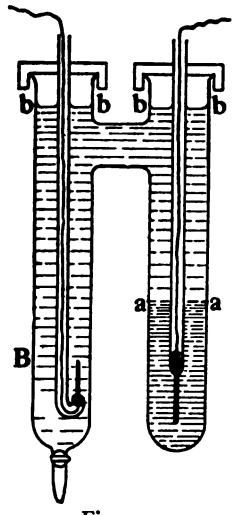


Fig. 74.

* Figure and experiment taken from "Physiko-Chemische Messungen," Ostwald-Luther-Drucker, pp. 504–5.

total quantity of electrical energy transported was 0.000 723; therefore the fraction transported by the $Ag^{\cdot}$ is $\frac{0.000\ 340}{0.000\ 723} = 0.470$, and the fraction transported by the NO_3' is $\frac{0.000\ 383}{0.000\ 723} = 0.530$; and these are, by definition, the transference (or transport) numbers for these ions.

If n_a is the transference number of the anion and n_c the transference number of the cation, then $n_a + n_c = 1$, or $n_c = 1 - n_a$.

Following is a short table of transference numbers of anions, from which the transference numbers of the corresponding cations may also be read by utilizing the above formula. The dilution, V, is given in terms of liters which must be taken to obtain a formula weight in grams, or half a formula weight in grams when the coefficient $\frac{1}{2}$ appears.

*V =	100	50	20	10	5	2	1	0.5
KCl, KBr, KI, NH_4Cl	0.506	0.507	0.507	0.508	0.509	0.513	0.514	0.515
NaCl	.....	.....	0.614	0.617	0.620	0.626	0.637	.....
KNO_3	.....	.....	.....	0.497	0.496	0.492	0.487	0.479
$AgNO_3$	0.528	0.528	0.528	0.528	0.527	0.519	0.501	0.476
KOH	.....	.....	.....	0.735	0.736	.....	.....	.....
HCl	.....	.....	0.172	0.172	0.172	0.173	0.176	.....
$\frac{1}{2}\ BaCl_2$	.....	.....	.....	.....	.....	.....	0.640	0.657
$\frac{1}{2}\ K_2CO_3$	.....	.....	.....	.....	.....	0.435	0.434	0.413
$\frac{1}{2}\ CuSO_4$	.....	0.62	0.626	0.632	0.643	0.668	0.696	0.720
$\frac{1}{2}\ H_2SO_4$	.....	.....	.....	.....	.....	0.182	0.174	.....

* The values in this table are taken from Kohlrausch and Holborn, "Leitvermogen der Elektrolyte," p. 201.

The transference numbers are evidently not wholly independent of the dilution. It has been observed, also, that temperature alters them, and Kohlrausch has shown that there is a tendency for them all to approach 0.5 at high temperatures. Let us suppose that at a certain dilution and temperature the cation moves 4 units distance while the anion moves 6. n_a then equals 0.6. Let us further suppose that at a higher temperature both move faster, for instance the cation 6 units to the anion 8. Then $n_a : n_c = 8 : 6$; but $n_a + n_c = 1$; therefore $n_a = 0.57$; that is, both transference numbers are nearer to 0.5.

Complex Ions. The methods described for determining transference numbers also enable us to decide as to what the ions probably

are into which a complex salt may be supposed to dissociate. For instance, AgCN dissolves in a solution of KCN, and the question arises, Are there $K^{\cdot}$ cations and also $Ag^{\cdot}$ cations in that solution? The chemical behavior is not that of a solution containing $Ag^{\cdot}$ and determination of concentration changes produced by electrolysis shows that the concentration of silver around the cathode is diminished more than corresponds to the amount of silver deposited on the cathode; therefore silver must have moved toward the anode, and so it must be part of an anion. It is thus plausible to assume the existence of a compound with a formula $KAg(CN)_2$ dissociating into $K^{\cdot}$ cations and $Ag(CN)_2'$ anions. Since silver is deposited on the cathode, we must assume that some $Ag^{\cdot}$ cations exist in the solution also, but their concentration must be exceedingly low, as rather sensitive qualitative chemical tests fail to detect them.

By this sort of reasoning we are led to assume the existence of the following salts, dissociating as indicated:

$$Na_2PtCl_6 \rightleftarrows 2\,Na^{\cdot} + PtCl_6''$$
$$NaAuCl_4 \rightleftarrows Na^{\cdot} + AuCl_4'$$
$$K_4Fe(CN)_6 \rightleftarrows 4\,K^{\cdot} + Fe(CN)_6''''$$
$$K_3Fe(CN)_6 \rightleftarrows 3\,K^{\cdot} + Fe(CN)_6'''$$

Amphoteric Electrolytes.* Apparently some substances are capable of dissociating in more than one way. These have been named amphoteric electrolytes. In acid solutions of lead salts the lead travels toward the cathode, in alkaline solutions it travels toward the anode. These are the facts, and the plausible explanation is that in the first case the lead is present as cations and in the second as anions. We are inclined to picture the probable mechanism something as follows: We make a solution of $Pb(C_2H_3O_2)_2$ and we may expect $Pb^{\cdot\cdot}$ cations and $C_2H_3O_2'$ anions. $H^{\cdot}$ cations and OH' anions are present also, due to a slight dissociation of water. Lead hydroxide being a weak base, a good deal of undissociated $Pb(OH)_2$ probably forms. This may dissociate in any or all of the four following ways:

1. $PbOH^{\cdot}$ cations and OH' anions;
2. $Pb^{\cdot\cdot}$ cations and 2 OH' anions;
3. $H^{\cdot}$ cations and $PbO(OH)'$ anions;
4. 2 $H^{\cdot}$ cations and PbO_2'' anions.

* Le Blanc, "Textbook of Electrochemistry," p. 79. G. Bredig, *Zeitschr. f. Elektrochem.*, 6, 33–37 (1899), and *Zeitschr. f. anorg. Chem.*, 34, 202–204 (1903). Walker, *Zeitschr. f. phys. Chem.*, 49, 82–94 (1904).

If a strong acid, such as HNO_3, is present, the concentration of the OH' is kept very low, due to the formation of undissociated water from $H^{\cdot}$ and OH', and so dissociation of types 1 and 2 will predominate. If a strong base, such as NaOH, is present, the concentration of the $H^{\cdot}$ is kept low according to similar reasoning, and then dissociation of the types 3 and 4 will predominate.

Kohlrausch's Rule. We can determine λ_∞ for strongly dissociated salts by simply increasing the dilution until λ reaches a maximum. At this point we have complete dissociation, and therefore the same carrying capacity in the form of ions, no matter what our salt may be. For we shall have half as many bivalent ions as univalent ions, one-third as many trivalent ions, and so forth; and we have seen that each valence (unit capacity factor of chemical energy) represents the ability to carry 96 500 coulombs. Hence we might at first expect to have the same value for λ_∞ for all completely dissociated salts. But this is not the case, and the λ_∞ values are found to be different. This is true even though only univalent ions, or only bivalent ions, are present.

Hittorf's work has made it exceedingly plausible that different ions carrying the same quantity of electrical energy move with different velocities. Evidently the conduction effected by one ion is the product of the quantity of electrical energy it carries, by the velocity with which it moves. Call this product for the cation U and for the anion V. Then the total conduction is the sum of these two quantities, or $U + V$. This is what is known as Kohlrausch's rule, first published in 1876.

If we limit ourselves to the consideration of equivalent quantities of completely dissociated substances (and these are the only conditions under which the rule as stated applies), the quantities of electrical energy on cations and anions are, by definition of what we mean by equivalent, exactly equal. Thus any differences in the values U and V must be solely differences in velocities. On this account the values U and V are commonly thought of as representing simply the velocity of migration of the cation and of the anion.

We may write $\lambda_\infty = U + V$, or, if only the fraction α is dissociated at the dilution v, we may write $\lambda_v = \alpha(U + V)$. Referring to the table on p. 441, we find λ_∞ for KCl, obtained by direct experiment (by determining λ at constantly increasing dilutions until the maximum is reached), is equal to 149.1. Referring to the table on p. 447, we find the transference number for Cl' at high dilution is

0.507, and then the transference number for $K^{\cdot}$ must be 0.493. Then 0.507 of 149.1 must be the fraction of the whole conduction effected by the Cl' anions, or $V = 75.6$ and $0.493 \times 149.1 = U = 73.5$, and $U + V = 73.5 + 75.6 = 149.1$, the equivalent conductivity of the completely dissociated salt.

According to the dissociation theory, the ions lead independent existences in solution, and so the conduction effected by unit quantity of an ion is entirely independent of what particular compound it came from. An equivalent quantity of $Ag^{\cdot}$ effects a quantity of conduction U, no matter what salt of silver is dissolved; and an equivalent quantity of NO_3' in the same way effects a quantity of conduction V, no matter what nitrate is dissolved. If we know U_{18} for $Ag^{\cdot}$ is 54.0 and V_{18} * for NO_3' is 61.8, we know that an equivalent weight in grams of $AgNO_3$, if completely dissociated, will have an equivalent conductivity $\lambda_\infty = U_{18} + V_{18} = 54.0 + 61.8 = 115.8$. In like manner we may calculate the λ_∞ values of all acids, bases, and salts if we know the individual values for the ions. The following table gives a number of these U and V values for 18° † in water solution, and their temperature coefficients, α.

	U	α		V	α
$Na^{\cdot}$	43.6	0.0244	Cl'	65.4	0.0214
$Ag^{\cdot}$	54.0	0.0229	I'	66.4	0.0213
$K^{\cdot}$	64.7	0.0217	Br'	67.6	0.0215
$H^{\cdot}$	318.0	0.0153	CHO_2'	47.0	.....
$NH_4^{\cdot}$	64.0	0.0222	$C_2H_3O_2'$	35.0	0.0238
$\frac{1}{2}Mg^{\cdot\cdot}$	46.0	0.0256	$\frac{1}{2}C_2O_4''$	63.0	.....
$\frac{1}{2}Zn^{\cdot\cdot}$	46.7	0.0251	$\frac{1}{2}SO_4''$	68.4	0.0227
$\frac{1}{2}Cu^{\cdot\cdot}$	47.3	.....	$\frac{1}{2}CO_3''$	70.?	0.027?
$\frac{1}{2}Cd^{\cdot\cdot}$	47.5	.....	IO_3'	33.9	0.0234
$\frac{1}{2}Sr^{\cdot\cdot}$	51.7	.....	ClO_3'	55.0	0.0215
$\frac{1}{2}Ca^{\cdot\cdot}$	51.8	.....	IO_4'	48.0	.....
$\frac{1}{2}Ba^{\cdot\cdot}$	55.5	0.0238	ClO_4'	64.0	.....
$\frac{1}{2}Pb^{\cdot\cdot}$	61.3	0.0243	NO_3'	61.8	0.0205
			OH'	174.0	0.0180

The temperature coefficients give the increase in U or V for each degree expressed as a fraction of the U or V value at 18°. For example, suppose we wish to calculate λ_∞ for KCl at 25°. We have U_{18} for $K^{\cdot} = 64.7$, then the increase upon raising the temperature 7° is $7 \times 0.0217 \times 64.7 = 9.97$, and U_{25} for $K^{\cdot} = 64.7 + 9.97 = 74.7$. In like manner we find V_{25} for $Cl' = 65.4 + 7 \times 0.0214 \times 65.4 = 75.4$, and so λ_∞ for KCl at 25° is $74.7 + 75.4 = 150.1$.

* The subscript 18 indicates that the values hold for 18°.

† Landolt, Börnstein, and Meyerhoffer, "Tabellen," p. 763 (1905).

That such a table can be constructed is a cogent argument in favor of the theory of the independence of the ions, *i.e.*, of the electrolytic dissociation theory. And the usefulness of such a table, compressing as it does an unusually large amount of information into small compass, is obvious. Besides this, it enables us to do some things we could not do without it.

It is not possible to determine the λ_∞ value for some substances because we cannot dilute enough to obtain a maximum value for λ. Practically, limits are reached because the quantity of the substance between the electrodes becomes so little, and the best water we can obtain conducts to a slight extent, and gases in the atmosphere, particularly carbon dioxide, dissolve and conduct. Yet we must know the λ_∞ value before we can apply the formula $\alpha = \frac{\lambda_v}{\lambda_\infty}$ to determine the degree of dissociation from the conductivity. Acetic acid is one such substance; but sodium acetate gives us a maximum value at reasonable dilutions, and from this we obtain the *V* value 35 for $C_2H_3O_2'$ in the table. Adding to this the *U* value for $H^{\cdot}$ (318) we have 353, which must be the λ_∞ value for acetic acid, which we would have obtained if we could have, experimentally. If, then, for an $\frac{n}{20}$ solution of acetic acid at 18° we find a conductivity of 0.318, the equ valent conductivity, λ_{20}, is 0.318×20, or 6.36, the fraction dissociated is $\frac{\lambda_{20}}{\lambda_\infty} = \frac{6.36}{353} = 0.018$, or we may say that acetic acid at that dilution and temperature is 1.8 per cent dissociated. The following short table may aid in fixing the interrelationship between these quantities in mind.

ACETIC ACID SOLUTIONS. 18°.

Equivalent normality.	Dilution in liters.	Conductivity $\times$ $10^4 = 10^4\,\chi$.	λ_v.	$\alpha = \frac{\lambda_v}{\lambda_\infty}$.	Per cent dissociated $= 100\,\alpha$.
0.05	20	3.18	6.36	0.018	1.8
0.167	5.97	5.84	3.50	0.0099	0.99
0.838	1.193	12.25	1.46	0.00414	0.414
1.688	0.592	15.26	0.904	0.00256	0.256
3.417	0.293	16.05	0.470	0.00133	0.133
5.194	0.1925	14.01	0.270	0.00076	0.076
10.66	0.0938	4.56	0.0428	0.000121	0.0121
14.25	0.0702	0.81	0.0057	0.000016	0.0016
17.41	0.0575	0.0004	0.0_323	0.0_365	0.0_365*

* Values in this table from, or calculated from, Landolt, Börnstein, and Meyerhoffer, "Tabellen," p. 741 (1905).

Remember that 0.0_42 is a convenient and much used condensation of 0.000 02,

The last horizontal line contains values for practically pure acetic acid, and we see that the dissociation of this is negligible. The table shows, also, how the conductivity goes first up, then down, but the equivalent conductivity and the degree of dissociation increase regularly as the dilution increases.

Actual Velocity of Ions. The numbers with which we have been dealing have all been expressions of the relative velocities of ions. We know something also about the rate at which they move expressed in centimeters per second.

A tube, about 40 cm. long and about 8 mm. in diameter, is bent at right angles near each end. Ten grams of gelatine are dissolved in 140 cm.^{3} of water with the aid of heat, 7 grams of sodium chloride and a few drops of slightly alkaline solution of phenolphthaleïn are added. The tube is filled with this mixture, which gelatinizes upon cooling. One end is inverted in a vessel containing a solution of cupric chloride (1 : 10) and a platinum cathode; the other end dips in a beaker of dilute hydrochloric acid, in which is a carbon anode.

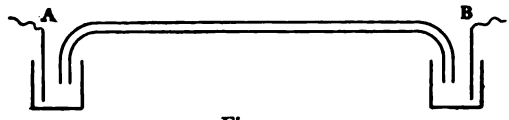


Fig. 75.

The general plan of the arrangement is illustrated in Fig. 75.* The hydrochloric acid diffuses into and along the tube, decolorizing the phenolphthalein, and the cupric chloride, diffusing in the opposite direction, displaces the red with a blue color. The rate at which these color changes progress, due to diffusion, must be determined. In one experiment the hydrochloric acid diffused 1 cm. in 1 hour, 2 cm. in 4 hours, and 5 cm. in 25 hours, while the cupric chloride diffused 0.5 cm., 1 cm., and 2.5 cm. in the same time intervals. These values correspond with the general law that the distance through which diffusion proceeds is directly proportional to the square root of the time.

A current is then sent through, from the hydrochloric acid to the cupric chloride, and both color boundaries move more rapidly. Subtracting the rates of diffusion from these greater rates gives us the velocities with which the ions move. These velocities are directly proportional to the electromotive force applied. (Twenty volts will

* More details regarding this experiment, first devised by Lodge, may be found in Lüpke, "Elements of Electrochemistry," p. 53.

cause the hydrogen ion boundary to move about 1.5 cm. in one hour.) For accurate results a more complicated apparatus has been devised. When all precautions have been taken, the directly obtained experimental results agree well with those calculated by the method described in the next paragraph.*

Calculation of Actual Velocities of Ions. Suppose we have a cell with electrodes 1 cm. apart and large enough to hold a solution containing an equivalent weight in grams of some completely dissociated substance. Suppose that when an electromotive force of one volt is applied at these electrodes 96.50 coulombs pass per second. Then this quantity passes any cross section of the circuit in the same time. Then ions enough to carry this quantity must have passed any cross section through the solution. Suppose for a moment the cations alone moved; then 0.001 of all present passed a given point in one second, for all present carry 96 500 coulombs, and 96.50 coulombs or $\frac{96.50}{96\,500} = \frac{1}{1000}$ of the total quantity. The ions are evenly distributed, to begin with at least, and might be likened to a procession 1 cm. long. At the above rate it would take the procession 1000 seconds to move 1 cm., or the actual velocity is 0.001 cm. per second.

The conductance of this cell we are considering is, by definition, the equivalent conductivity of the dissolved substance. It is clear, then, that $\frac{\lambda_\infty}{96\,500}$ is the fraction of an equivalent weight in grams of ions which pass a given cross section in one second. But part of this total transfer is due to cations moving in one direction, and the rest is due to anions moving in the opposite direction. The relative velocities we have determined and designated with U and V, and we know $\lambda_\infty = U + V$. Then $\frac{U}{96\,500}$ is the fraction of an equivalent weight in grams of the cation which passes a given point in one second, and $\frac{V}{96\,500}$ is the fraction of an equivalent weight in grams of the anion which passes a given point in one second. In each case the equivalent weight is distributed evenly throughout the 1-centimeter

* For descriptions of apparatus and methods for determining these actual velocities see: W. C. D. Whetham, *Trans. Roy. Soc.*, **184**, 337–359 (1893). Orme Masson, *Trans. Roy. Soc.*, **192**, 331–350 (1899). B. D. Steele, *Zeitschr. Electrochem.*, **7**, 618–622 (1901) and *Trans. Roy. Soc.*, **198**, 105–145 (1902).

layer; as has been suggested, like a marching column 1 cm. long. Therefore $\frac{U}{96\,500}$ and $\frac{V}{96\,500}$ are respectively the fractions of a centimeter traversed by cations and anions per second. The actual velocity of any ion, in cm. per second, under the influence of a potential fall of 1 volt per cm., is thus its U or V value divided by 96 500.

Referring to the table (p. 450), we find U for $K^{\cdot} = 64.7$. Then $\frac{64.7}{96\,500} = 0.000\,670\,5$ cm. per second is its actual velocity. U for $H^{\cdot}$ is 318. Therefore, the velocity with which it moves under the influence of a difference in potential of 1 volt per cm. is $\frac{318}{96\,500} = 0.003\,294$ cm. per second.

Since $C = \frac{E}{R}$, doubling the e.m.f., while the resistance remains the same, doubles the current, and consequently must double the velocities of all ions engaged in the conduction. Therefore the velocities are directly proportional to the e.m.f. So to obtain the velocity of a given ion under other driving forces we must multiply the velocity obtained as above by the fall in potential per cm. For instance, if our cell has electrodes 40 cm. apart and we apply an e.m.f. of 20 volts (these are about the conditions in the experiment described on p. 452), the fall in potential is 0.5 volt per cm., and we should expect the hydrogen ions to travel about $0.5 \times 0.003\,294 = 0.001\,647$ cm. per second. This is just about what we observe when the experiment is carried out carefully.

Effect of Viscosity on the Velocity of Ions. The smaller the particles the slower they fall out under the influence of gravitation, as was brought out in Chapters X and XIX. Their motion is retarded by the friction between them and the surrounding medium. Whatever increases the viscosity of the solvent must also retard the movement of the ions. An addition of alcohol to water is found to increase its viscosity and to diminish the velocity of the ions. Nearly anything, upon dissolving, increases the viscosity of water and consequently causes the ions to move more slowly.

Electrical Endosmosis. If a cell filled with water is divided by a porous porcelain diaphragm into an anode and a cathode compartment and a high e.m.f., say 50 to 100 volts, is applied, the level of the water rises in the cathode compartment. The water seems to be forced through the capillaries of the diaphragm, and the effect is the more marked the less the conductivity of the water. This phe-

nomenon is called electrical endosmosis, no doubt because a membrane is an essential part of the apparatus; but this is another of our rather frequent misnomers. One hardly dares say any phenomenon has nothing whatever to do with another, but "electrical endosmosis" is no more nearly related to osmosis than is the fact that like charges repel each other.

Cataphoresis. Under the influence of a difference in potential, suspended particles move through a liquid. This phenomenon is called cataphoresis. Most particles suspended in water, such as clay for instance, behave as if carrying negative charges and move toward the anode. The still smaller particles in colloidal solutions exhibit the same behavior. Colloidally dissolved (or suspended) Pt, Au, Ag, Se, Cd, Sb, sulphides, silicic acid, etc., move toward the anode; hydroxides such as $Fe(OH)_3$ and $Al(OH)_3$ and other substances such as hæmoglobin and methyl violet move toward the cathode. White of egg, long dialyzed, moves neither way, but if we add a drop of an acid it moves toward the cathode, if we add a drop of an alkali it moves toward the anode.

It is interesting to note we have here the reverse of what we should expect from the more familiar instances of electrolysis. When a salt dissociates we have good reason to suppose the metal ions carry positive charges; but colloidally dissolved particles of many metals behave as if they carried negative charges.

Electrostenolysis. When exceedingly fine capillaries such as cracks in a glass tube divide an electrolytic cell into two compartments, it sometimes happens that metals are deposited as such on the walls of the capillaries. This is called electrostenolysis.

The theories pertaining to cataphoresis and electrostenolysis are involved, uncertain, and incomplete, and would therefore require too much space to be included here.*

Ostwald's Dilution Law and the Dissociation Constant. Ostwald's dilution law, namely, that if α = fraction dissociated and v = dilution of a binary electrolyte, $\frac{\alpha^2}{v(1-\alpha)} = K$, was given in Chapter XXVI. It was there said that this equilibrium constant, called the dissociation constant, is a measure of the "affinity" of a

* For further information and extensive bibliographies (for many investigations have been devoted to this subject) see Le Blanc, "Electrochemistry"; Wolfgang Ostwald, "Grundriss der Kolloidchemie"; H. Freundlich, "Kapillarchemie."

substance, and it was stated that the formula holds well for weakly dissociated substances but not well for strongly dissociated substances. The Rudolphi-van't Hoff empirical formula for the latter was given also in that connection.

We now know that $\alpha = \frac{\mu_v}{\mu_\infty}$. Substituting in the above formula, we obtain

$$\frac{\left(\frac{\mu_v}{\mu_\infty}\right)^2}{v\left(1 - \frac{\mu_v}{\mu_\infty}\right)} = K = \frac{\mu_v^2}{\mu_\infty(\mu_\infty - \mu_v)v}.$$

So we need only to determine the values of μ_v and μ_∞ to calculate K. Remember that v is sometimes expressed in cm.^{3}, sometimes in liters. The latter unit was used in calculating the dissociation constants in the table in Chapter XXVI. The unit chosen for v alters the position of the decimal point but not the significant figures.

A Deduction from Ostwald's Dilution Law. Suppose a weakly dissociated substance, for which the formula holds, is 50 per cent dissociated. Then, inserting this value in the formula, we have, $\frac{(\frac{1}{2})^2}{\frac{1}{2}v} = K$, or $2K = \frac{1}{v}$. The concentration is the reciprocal of the dilution, and so twice the dissociation constant is always the concentration at which the substance is just half dissociated.

The Dissociation Constant and Chemical Constitution. The dissociation constant of formic acid is 0.0214, of acetic acid is 0.0018, of propionic acid is 0.001 34. Their formulæ differ by CH_2, and so we may say the addition of CH_2 diminishes the strength of an acid. But this effect appears to cease after the first three of this homologous series.

The dissociation constants of butyric and isobutyric acids are, 0.001 49 and 0.001 44; very nearly the same. This is odd, for generally such differences of constitution are accompanied by greater differences in properties.

Substitution of chlorine in acetic acid much increases the strength of the acid. At 25°, 100 000 K,

For acetic acid, is	0.0018
For monochloracetic acid,	0.155
For dichloracetic acid,	5.14
For trichloracetic acid,	121.

The second of these acids is about 86 times as strong as the first, the third about 33 times as strong as the second, the fourth about 23 times as strong as the third.

The effect of substituting other substances or groups is shown below (100 000 K at 25°).

Monobromacetic acid, CH_2BrCO_2H	0.138
Cyanacetic acid, $CH_2(CN)CO_2H$	0.370
Sulphocyanacetic acid, $CH_2(SCN)CO_2H$	0.265
Thioglycollic acid, $CH_2(SH)CO_2H$	0.0225
Glycollic acid, $CH_2(OH)CO_2H$	0.0152
Glyoxalic acid, $CH(OH)_2CO_2H$	0.0474

The value for monobromacetic acid is nearly the same as that for monochloracetic acid. Cyanacetic acid appears to be much stronger, in spite of the fact that hydrocyanic acid is so weak an acid it hardly deserves the name. This leads us to think that HCN should not be compared with the halogen acids, as is customary, but rather should be considered as an imide compound.*

The OH group and the SH group both increase the strength of an acid. The substitution of two OH groups strengthens an acid, but the second is not so effective as the first. In the same way, the effect of the second substituted chlorine is not so great as the effect of the first.

We can also measure the difference in effects when one thing occupies different positions in isomeric compounds. For example, at 25°, 100 000 K,

For benzoic acid, is	0.0060
For orthoxybenzoic acid (salicylic),	0.102
For metaoxybenzoic acid,	0.0087
For paraoxybenzoic acid,	0.00286

Starting from benzoic acid and putting an hydroxyl group in the ortho position increases the strength of the acid considerably; putting it in the meta position makes little change, and putting it in the para position diminishes the strength.

It is evident that the conductivity method and dissociation constant may be utilized to determine which of a number of possible isomers we may happen to have.†

* H–C ≡ N (acid). C ≡ N–H (imide).

† For additional information see the extensive tables in Ostwald's "Lehrbuch der Allgemeinen Chemie," in Landolt, Börnstein, and Meyerhoffer's "Tabellen," and in Kohlrausch and Holborn's "Leitvermögen der Elektrolyte."

Where three or more ions result from dissociation, the formula for the dissociation constant is more complicated. Some such cases have been investigated and the results agree within reasonable limits with the theory. The simple formula we have been discussing applies fairly well without alteration to a number of dibasic acids, if they are not too dilute. This is an argument in favor of the theory that these substances dissociate stepwise; first we have one H' cation and one univalent anion, and only later do we begin to have appreciable quantities of the bivalent anion to each of which correspond two H' cations.

Calculating the Dilutions at Which Two Acids are Equally Dissociated. When two acids are equally dissociated, α, the degree of dissociation for one, is equal to α_1, the degree of dissociation for the other. If K and v are the dissociation constant and dilution for the first, and K_1 and v_1 these quantities for the second, we have $\frac{\alpha^2}{(1-\alpha)v} = K$ and $\frac{\alpha_1^2}{(1-\alpha_1)v_1} = K_1$; and since $\alpha = \alpha_1$, $\frac{\alpha^2}{1-\alpha} = \frac{\alpha_1^2}{1-\alpha_1}$, or $Kv = K_1v_1$. Substituting the known values for K and K_1, we obtain at once what we want,— the values for v and v_1 at which the two acids are dissociated to the same degree.

Since $Kv = K_1v_1$, $\frac{K}{K_1} = \frac{v_1}{v}$, or the ratio between the dilutions for equal dissociation is a constant. For instance, if we have two acids equally dissociated and double or treble the dilution in each case, the resulting solutions will be equally dissociated.

Calculating Dilution Necessary for a Definite Degree of Dissociation. Ostwald's dilution formula enables us to calculate the dilution required for a definite degree of dissociation, if we know the dissociation constant K.

For instance, we wish to know the dilution at which acetic acid (25°) is 10 per cent dissociated. $K = 0.0_718$ and $\alpha = \frac{1}{10}$. We have $\frac{(0.1)^2}{(1-0.1)v} = 0.0_718$ or $v = \frac{(0.1)^2}{(1-0.1)\,0.0_718} = 617\,300$ cm.^{3} or 617.3 liters; *i.e.*, an $\frac{n}{617.3}$ solution of acetic acid is 10 per cent dissociated.

Isohydric Solutions. Solutions are called isohydric when they do not affect each other's degrees of dissociation upon being mixed, and when the conductivity of the mixture is the mean of those of the two solutions.

A solution of sodium acetate contains $Na^{\cdot}$ cations and CH_3COO' anions and undissociated molecules. A solution of acetic acid contains $H^{\cdot}$ cations, CH_3COO' anions and undissociated molecules. The acetate ion is common to both solutions. Let $C_{Na\cdot}$ represent the concentration of the $Na^{\cdot}$, let A' represent the acetate ions and $C_{A'}$ their concentration in the sodium-acetate solution, and let C_{NaA} represent the concentration of the undissociated sodium acetate. Applying the law of mass action, we have: $C_{Na\cdot} \times C_{A'} = K_1 C_{NaA}$. Let $C_{H\cdot}$ represent the concentration of the $H^{\cdot}$ cations, C_{HA} the concentration of the undissociated molecules of acetic acid, and $[C_{A'}]$ the concentration of the acetate ions in the acetic-acid solution. We may then write $C_{H\cdot} \times [C_{A'}] = K_2 C_{HA}$.

Suppose we mix x liters of the salt solution with y liters of the acid solution. The total volume of the solution becomes $x + y$ liters, and, assuming for the moment that the original quantities of the different ions do not change, we shall have the following concentrations:

$$\frac{x}{x+y} C_{Na\cdot}; \quad \frac{x}{x+y} C_{A'}; \quad \frac{x}{x+y} C_{NaA};$$

also

$$\frac{y}{x+y} C_{H\cdot}; \quad \frac{y}{x+y} [C_{A'}]; \quad \frac{y}{x+y} C_{HA}.$$

The A' ion being common to both, the equilibrium equation for the salt becomes $\frac{x}{x+y} C_{Na\cdot} \left(\frac{x}{x+y} C_{A'} + \frac{y}{x+y} [C_{A'}] \right) = K_1 \frac{x}{x+y} C_{NaA}$. This simplifies to $C_{Na\cdot} \left(\frac{x C_{A'} + y [C_{A'}]}{x+y} \right) = K_1 C_{NaA}$. If $C_{A'} = [C_{A'}]$ we have $C_{Na\cdot} \left(\frac{(x+y) C_{A'}}{x+y} \right) = K_1 C_{NaA}$ or $C_{Na\cdot} C_{A'} = K_1 C_{NaA}$; *i.e.*, our original expression for the equilibrium in the salt solution, which means that the degree of dissociation of the salt has not been altered by adding the solution of acid.* This is what we mean by the term isohydric. Thus we see that in order that solutions shall be isohydric the concentration of the common ion must be the same in each.

If there is no common ion, it is impossible for two solutions to be isohydric; upon mixing, each must affect the degree of dissociation of the other.

In the case of two acids, the hydrogen ion is common to both, and the only condition under which they will be isohydric is when the con-

* Analogous equilibrium equations written for the acid lead to identical results.

centration of the H' is the same in both solutions. Acetic acid is a weak acid, but slightly dissociated, and so the concentration of the H' is small. Hydrochloric acid is a strong acid, much dissociated, consequently to obtain isohydric solutions of these two we must take a fairly concentrated solution of acetic acid and a much more dilute solution of hydrochloric acid.

The Basicity of Acids. A regularity has been noticed for which there is no satisfactory explanation, but which enables us to determine the basicity of an acid. It has been observed that the equivalent conductivity of the sodium salts of monobasic acids increases from a dilution of $v = 32$ liters to $v = 1024$ liters by close to 10 units. Dibasic acids show an increase of about 20 units; tribasic an increase of 30 units, and so on. We can express this regularity in a formula; $\frac{\lambda_{1024} - \lambda_{32}}{10}$ = the basicity of the acid.

	λ_{1024}	λ_{32}	Difference.	Basicity of the acid.
Sodium acetate.....	90.6	80.5	10.1	1
Sodium oxalate.....	122.2	101.1	21.1	2
Sodium citrate.....	117	87	30	3

Use of the Basicity Rule to Determine the Molecular Formula. An acid was being investigated which was insoluble in the usual solvents. Therefore the boiling-point and freezing-point methods could not be applied. It decomposed on heating. Therefore vapor-density methods were out of the question. Combustion gave the percentage composition and the empirical formula, but left the molecular formula uncertain.

A weighed amount of the solid acid was exactly neutralized with $\frac{n}{32}$ NaOH solution and the conductivity of this solution at this dilution and at the dilution $v = 1024$ liters was taken. The difference was 10 units; it was reasonable to suppose the acid to be monobasic and the molecular formula could then be written.

Pure Water. The more carefully water is purified, the less its conductivity. Kohlrausch and Heydweiller succeeded in obtaining such pure water that further efforts to purify did not diminish its conductivity. Extraordinary precautions were necessary. Having obtained the purest water possible in contact with the air, it was put

in a retort, on which the cell containing the electrodes was sealed. The whole apparatus was evacuated and then sealed. A small portion of the water was distilled over, exceedingly slowly, into the measuring cell. The conductivity, χ, of their best water at 18°, was 0.0384×10^{-6}. The best water which can be obtained in contact with the air has a conductivity about twenty times this, or 0.8×10^{-6}. Water is considered good enough for ordinary measurements by the conductivity method if its conductivity is not above 2×10^{-6}. Distilled water such as is used in analytical work generally has a conductivity around 15×10^{-6}. The temperature coefficient of purest water is surprisingly large, about 5.8 per cent per degree as compared to 2–2.5 per cent for the majority of salt solutions.

Degree of Dissociation of Water. From the table (p. 450) we have the U and V values, for H', 318, for OH', 174. Therefore a formula weight in grams of completely dissociated water, between electrodes 1 cm. apart, would give us a conductance $318 + 174 = 492$. One cm.^{3} of purest water between electrodes 1 cm. apart gave a conductance of 0.0384×10^{-6}. A liter would have given 1000 times this, or 0.0384×10^{-3}. Therefore the fraction of a formula weight in grams of water which is present, dissociated into its ions at 18°, in 1 liter, is,

$$\frac{0.0384 \times 10^{-3}}{492} = 0.7803 \times 10^{-7}.$$

Theoretically at least, a second dissociation is possible wherein OH' may dissociate to H' and O''. We have learned that the analogous second step in dissociation of dibasic acids is a negligible quantity until the first dissociation has proceeded rather far. It is therefore reasonable to suppose that this second dissociation in the case of water is quite negligible under all known conditions.

Determining Solubility of Difficultly Soluble Salts. The conductivity method gives us a rapid and convenient way to estimate the solubility of difficultly soluble substances. The reasoning and calculation may be demonstrated by an example.

Kohlrausch* determined the conductivity of some water as 1.16×10^{-6}; he saturated this with silver chloride and then found the conductivity 2.40×10^{-6}, all at 18°. $2.40 \times 10^{-6} - 1.16 \times 10^{-6} = 1.24 \times 10^{-6}$ is evidently the conductivity due to the presence of the silver chloride. The dilution is so very great we may assume that

* Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," p. 133.

all the AgCl present is dissociated into $Ag^{\cdot}$ and Cl'. From the table (p. 450) we find the equivalent conductivity values, 54 for $Ag^{\cdot}$ and 65.4 for Cl'. This means that if we had a formula weight in grams of AgCl, completely dissociated between electrodes 1 cm. apart, we should find a total conductance of $54 + 65.4 = 119.4$. A conductance of 1.24×10^{-6} was found for the $Ag^{\cdot}$ ions + the Cl' ions in 1 cm.^{3} between electrodes 1 cm. apart. A liter would have given a conductance 1.24×10^{-3}. Therefore $\frac{1.24 \times 10^{-3}}{119.4}$ is the fraction of a formula weight in grams of AgCl present in 1 liter of a solution saturated at 18°. The formula weight of AgCl is 143.4. Therefore $\frac{1.24 \times 10^{-3}}{119.4} \times 143.4 =$ grams AgCl dissolved in 1 liter $= 0.001\,49$. We thus have found the solubility of AgCl to be 1.49 mg. per liter.

The "Hardness" of Water. Kohlrausch has called attention to the fact that the conductivity method is well adapted to estimating the approximate "hardness" of water. It so happens that the equivalent conductivities of most salts such as constitute the "hardness" of water, in $\frac{n}{100}$ solutions, are in the neighborhood of 100. Then the conductivity of the water, χ, times 1000, divided by 100, gives approximately the number of gram equivalents of salt present per liter, or $10\,000\,\chi$ is approximately the number of milligram equivalents present per liter.

Conductivity of Nonaqueous Solutions. The conductivity of solutions in solvents other than water has been the subject of many extensive investigations in recent years. It is not possible to enter upon the details, and mention of a few general conclusions must suffice.* The conditions are much more complicated than in the case of water solutions. Different solvents appear to have different

* An admirable survey of the subject and all pertinent references may be found in "Elektrochemie der nichtwässrigen Lösungen," by G. Carrara, translated from Italian into German by K. Arndt. "Sammlung Chemischer und chemisch-technischer Vortraege," Vol. XII, pp. 404–446 (1908).

We owe a remarkably painstaking and comprehensive series of investigations of all aspects of the topic to P. Walden, "Uber organische Lösungs-und Ionisierungsmittel." *Zeitschr. f. phys. Chem.*, **46**, 103–188 (1903); **54**, 129–230 (1906); **55**, 207–249, 281–302, 683–720 (1906); **58**, 479–511; **59**, 192–211, 385–415; **60**, 87–100 (1907); **61**, 633–639 (1908).

Other investigators too numerous to mention have added to our knowledge of certain phases of the subject.

abilities to dissociate solutes. This dissociating power seems to run parallel with the dielectric constant of the solvent.

Dielectric Constant. Faraday discovered in 1837 that the attraction, or repulsion, between two electrical charges was different in different media. The media in this connection are sometimes called dielectrics. If E_1 and E_2 are two charges which are a distance r apart, the attraction, or repulsion, K, equals $\frac{E_1E_2}{r^2D}$, where D represents this specific property of the medium and is called the dielectric constant. The attraction is then proportional to the product of the charges and inversely proportional to the dielectric constant and the square of the distance apart. The capacity of a condenser (in its simplest form a condenser consists of two parallel metallic plates separated by some insulating material) is directly proportional to the dielectric constant of the insulating material. Therefore specific induction capacity is another term for the same quantity as is denoted by dielectric constant.*

Call the capacity of a condenser when air separates the plates equal to unity. If pure water is substituted for air its capacity will be found to be 80. Eighty is, therefore, by definition, the dielectric constant of water. Call the attraction between two charges separated by air equal to unity. Substitute ethyl alcohol for air and the attraction will fall to $\frac{1}{25}$. Twenty-five is, therefore, by definition, the dielectric constant of ethyl alcohol.

The following table compares the dielectric constants of some solvents and their abil'ty to dissociate solutes.†

Solvent.	Dielectric constant.	Electrolytic dissociation.
Benzene	2.3	Exceedingly small conductivities indicate traces of dissociation.
Ether	4.1	Distinct and measurable conductivities.
Alcohol	25	Fairly strong dissociation.
Formic acid	62	Strong dissociation.
Water	80	Very strong dissociation.
Hydrocyanic acid	96	Very strong dissociation.

The dielectric constant is, as it were, a measure of the insulating ability of a substance; in a sense, the reverse of the conducting ability.

* For a description of Nernst's simple method for determining dielectric constants see Le Blanc, "Electrochemistry," p. 146.

† W. Nernst, "Theoretische Chemie," sixth edition, p. 379.

Thus it is entirely reasonable to suppose that when a substance is once dissociated the ions will attract each other less, tend less to recombine, the higher the dielectric constant. We do not know what causes a substance to dissociate in any solvent. We may assume a form of motion within the molecule tending to cause it to break apart, similar to the motion we assume in the kinetic theory of gases causing molecules of gases to fly about and fill completely any containing vessel. We cannot account for the existence of the second form of motion any better than we can for the first.

The conduction of electrical energy through a solution depends, not only on the degree of dissociation, but also on the velocity with which the ions move. This in turn must be a function of the viscosity of the medium through which they move. Walden* succeeded in demonstrating that the conductivity of his typical substance, tetraethyl ammonium iodide, $N(C_2H_5)_4I$, varied inversely as the viscosity of between forty and fifty different solvents in which he investigated it.

In many cases the solvent and solute combine to form new substances, and these may dissociate in a variety of different ways. It is hardly to be wondered at, with so many factors entering into the problems, that some facts were found which, at first, appeared to invalidate the assumption of electrolytic dissociation in some of these solvents. But when these other factors have been allowed for, the results harmonize with those obtained with water solutions. Carrara† closes his careful consideration of all the evidence as follows: "We may conclude, in spite of all uncertainties, that there is no essential difference between water solutions and solutions in other solvents. The theory of electrolytic dissociation may be applied to solutions in solvents other than water if corrections are applied for concomitant phenomena which are much more complicated in these than in water solutions."

Conductivity of Solid and Fused Salts. Solid salts are very poor conductors, but their ability to conduct increases rapidly with the temperature; and some, near their melting points but still solid, are good conductors. There is no abrupt and large increase in the conductivity upon melting. Fused KCl at 750° has an equivalent conductivity of 90.6. The equivalent conductivity of an $\frac{n}{50}$ KCl solution at 18° is 119.8.

* *Loc. cit.*

† *Loc. cit.*, p. 440.

The presence of small quantities of a second salt as an " impurity " much increases the conductivity of a solid salt even at low temperatures. This is analogous to the behavior of solutions and leads us to believe there must be similarities between the condition of the solid impurity and the dissolved solute. We indicate this by use of the term " solid solution," as was brought out in Chapter XVIII.*

* For a comprehensive treatment of this subject see Richard Lorenz, "Die Elektrolyse geschmolzener Salze," Vol. I, 213 pp., Vol. II, 257 pp. (1905).

CHAPTER XXIX

ELECTROCHEMISTRY — II

THE INTENSITY FACTOR

Electromotive Force. We shall now study the intensity factor of electrical energy, electromotive force, also called the potential. As its name implies, this is the factor which determines whether electricity will move from one place to another. If two charged bodies in contact have the same electromotive force, though the quantity of electricity contained by one be thousands of times greater than that contained by the other, no transference of electricity will take place.

Measuring Electromotive Force. Suppose we wish to determine the electromotive force of some cell. Let R_1 equal the internal resistance of the cell, and R_2 the resistance of the outside circuit. Then $C = \frac{E}{R_1 + R_2}$. We can make R_2 so large that R_1 in comparison with it is small enough to be neglected. Measure C with a delicate amperemeter. Then put some other cell with a different electromotive force, E_1, in place of the first, and, keeping R_2 constant, measure the new C_1. Then $C = \frac{E}{R_2}$ and $C_1 = \frac{E_1}{R_2}$. Then $R_2 = \frac{E}{C} = \frac{E_1}{C_1}$. Or, $EC_1 = E_1C$. Or $E : E_1 = C : C_1$. In words, the current varies directly with the electromotive force. If the electromotive force of one of the cells is known, that of the other may be calculated.

If we wish to eliminate the error due to the internal resistance, we may proceed as follows: Connect the two cells so that their electromotive forces work in the same direction, and measure the current, C. Then connect them so that their electromotive forces are opposed, and measure the current, C_1. We have the two equations, $C = \frac{E + E_1}{R}$ and $C_1 = \frac{E - E_1}{R}$. Or, $R = \frac{E - E_1}{C_1}$, and substituting, $\frac{E + E_1}{E - E_1} = \frac{C}{C_1}$. Solving for E, we have, $E = E_1 \frac{C + C_1}{C - C_1}$.

The Poggendorff Compensation Method. The Poggendorff compensation method depends upon the fact that electromotive force falls along a circuit from one end to the other directly proportionally to the resistance. We speak of the " fall in potential " or " potential gradient."

The instruments and connections are indicated in Fig. 76. A source of electromotive force, *D* in the figure, greater than that which we wish to measure, is connected to the two ends of a high resistance wire, *AB*, stretched on a meter stick. The cell to be measured, *G*, is connected in such a way that its potential is opposed

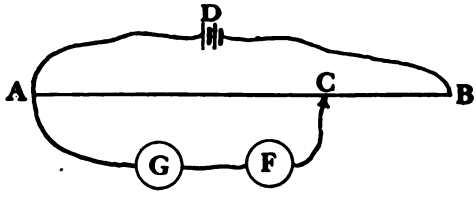


Fig. 76.

to that of *D*, and by means of the movable knife-edge contact, *C*, more or less of the main circuit is included within its circuit. A delicate electrometer (a name for any instrument which will detect a small current) is inserted at *F*. The current from *D* flows through *A*, past *C* to *B* and back to *D*. The current from *G* passes through the electrometer, *F*, to *C*, to *A*, and back to *G*. The knife-edge *C* is moved to and fro until no current whatever passes through *F* in either direction. Then the potential difference between *A* and *C* due to *D* must be exactly equal and opposite to the potential difference at the same places due to *G*. This is the entire electromotive force of *G* if no current is passing. The potential difference between *A* and *B* due to the source *D* is known. The potential between *A* and *C* is the same fraction of that between *A* and *B* as the resistance from *A* to *C* is of the resistance from *A* to *B*. The electromotive force of cell *G* is thus found.

This is known as a zero method for obvious reasons. It is essential that no current should flow through the *G*–*F* circuit; otherwise some current from *D* would pass that way, we should have a branching circuit, and the resistance from *A* to *C* would not be that read off on the meter stick. Moreover, the potential between *A* and *C* would not be the electromotive force of the cell *G*.

Potentiometer. Very few cells show a constant potential when closed through a small resistance for any length of time. It is advisable to use coils of wire with a total resistance of 1000 ohms or more. A storage cell closed through as much resistance as this maintains a potential so constant we cannot detect an alteration in days. Resistance boxes designed for this use are arranged in such a way that we can alter the position of the movable contact *C* in very small steps. Such an instrument is called a potentiometer, and some are elaborate and expensive.

Practically, we insert an accurately known electromotive force, a standard cell, in place of *G* and calculate the potential from *A* to *B*. We then take this out and substitute the cell to be measured.

Standard Cells. It is therefore a matter of most fundamental importance for electrical measurements to devise a cell which will give some accurately known e.m.f. and which may be reproduced as readily as possible. In view of the use to which it is to be put, it need not be capable of furnishing much of any current. Careful study has been given to this problem, with the result that we have specifications for two standard, or normal, cells, either of which serves the purpose well.

Weston, or Cadmium, Standard Cell. Most used at present is the so-called Weston, or cadmium, cell. Fig. 77 is about half the usual size. A platinum wire is sealed through the bottom of each limb of an H-shaped glass cell. *A* represents a small mass of 10 to 15 per cent cadmium amalgam; *B*, a layer of cadmium-sulphate crystals.* *C* is a small quantity of pure mercury, over which is placed a layer, *D*, of solid mercurous sulphate made into a paste with a saturated solution of $CdSO_4$. The rest of the cell is filled with a saturated solution of $CdSO_4$ and cadmium sulphate crystals and the openings are sealed with layers of

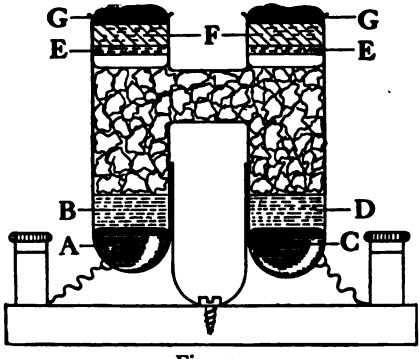


Fig. 77.

* Crystallized cadmium sulphate has the formula, $CdSO_4 \cdot 8/3\ H_2O$. It may be obtained by protracted boiling of finely divided cadmium with a dilute solution of mercurous sulphate.

paraffin, *E*, cork, *F*, and sealing wax, *G*. The best way to close the cell is by sealing off the tubes in the blast lamp. In this form the cell will show the definite e.m.f. of 1.0183 volts at 20° unaltered for years.*

Temperature Coefficient of Cadmium Standard. Besides its ready reproducibility, this cadmium cell has the great advantage that its temperature coefficient is so small it may be ignored in most measurements. By temperature coefficient we mean the change in e.m.f. produced by changing the temperature one degree. The e.m.f. of the cadmium standard is, $1.0183 - 0.000\,038\,(t - 20)$ volts, where t is the temperature of the experiment. The e.m.f. is a little lower, the higher the temperature; but two or three degrees will not make a change falling within the limits of experimental error of most measurements.

Clark, or Zinc, Standard Cell. Until about 1904 the Clark, or zinc, standard cell was considered the most reliable reference cell. Fig. 77 may be taken to represent this as well as the cadmium cell if the following substitutions are made: *A* represents a mass of zinc amalgam, *B* crystalline zinc sulphate, and the rest of the cell is filled with a saturated solution of $ZnSO_4$ and crystals of zinc sulphate. The chief disadvantage of this cell, as compared to Weston's, is its relatively large temperature coefficient. Its e.m.f. may be formulated as follows:

$$1.4328 - 0.001\,19\,(t - 15) - 0.000\,07\,(t - 15)^2 \text{ volts.}$$

Other cells have been suggested, and in some cases have been adopted, but the above are preëminently what are meant by "standard cells." †

The Electrometer. A good, sensitive galvanometer is the best instrument to use to determine when no current is passing, in connection with Poggendorff's method. But there is another sufficiently sensitive contrivance, known as Lippmann's capillary electrometer, which it is within the capacity of anyone to make at small expense. Partly on this account, but more because it introduces certain interesting facts and theories, it will be described at some length.

* Established as the legal value by an international committee. *Zeitschr. f. phys. Chem.*, **75**, 674 (1911).

† For additional information regarding the technique in constructing these cells see Ostwald-Luther, "Physico-chemische Messungen." Also watch the current literature, for these fundamental values are still a favorite subject of research for our Bureau of Standards, the Reichsanstalt in Germany, and a number of independent investigators.

Surface Tension of Mercury. When mercury is covered with some electrolytes, as for instance dilute sulphuric acid, its surface tension is decreased. The following experiment is exceedingly interesting and easily carried out.

Place about 6 to 8 cm^3 of mercury in a small evaporating dish. Pour over it dilute sulphuric acid (1 : 10) containing a trace of potassium dichromate, sufficient to give the solution a light lemon-yellow color. The drop of mercury flattens out, thus showing that its surface tension has decreased. Touch it with an iron wire and it contracts suddenly. Fix the wire in such a position that this contraction breaks the contact. Then the mercury flattens out once more, but once more comes in contact with the wire and promptly shrinks. In this way we can obtain a rhythmic pulsation of the mercury which is very surprising to watch. This is by no means a new phenomenon. It was first noticed by Henry in 1800, but first satisfactorily explained by Lippmann in 1873, and by Helmholtz in 1879.

Lippmann found that, when he added minus electricity to the mercury, its surface tension increased and the drop shrank. By applying enough minus electricity, he could get the drop back to its original form. When he applied more, the drop once more expanded. When the iron wire in the above experiment comes in contact with the mercury, it gives minus electricity to the mercury, because it dissolves, going into solution as ions with plus charges. This, of course, leaves the wire charged minus, and it is this minus electricity which goes over to the mercury. At the same time the chromic acid in the solution is reduced to chromium sulphate, $Cr_2(SO_4)_3$.

Lippmann concluded that the surface of contact between mercury and the electrolyte is a seat of difference of electromotive force; that the surface tension is intimately connected with this difference of potential; that, in fact, one is a function of the other; so that if we alter one, the other alters.

Lippmann's Capillary Electrometer. He made use of this principle to construct a sensitive electrometer. One of the most convenient of the numerous forms of this instrument is shown in Fig. 78, which is about one-half actual size. The bulb at *A* is half filled with mercury and a platinum wire sealed through the glass establishes electrical connection. Mercury is poured into the other side until it stands at *B* in that tube and at *C* in the fine capillary. *C* is considerably below *B*, owing to the capillary depression of mercury. Dilute sulphuric acid (1 : 6 by volume) fills the rest of the apparatus

and is in contact with mercury at C and at A. A wire dipping into the mercury at B establishes the other electrical connection.

The position of the mercury at C is determined by its surface tension; if this surface tension is made greater, the meniscus will go down; if it is made less, it will go up. If this instrument is placed in a circuit and minus electricity enters at B, this increases the surface tension at C and the meniscus moves downward. If plus electricity enters at B, this diminishes the surface tension, and the meniscus rises. The amplitude of the movement is, of course, a function of the diameter of the capillary; the smaller the capillary the greater the movement. Watching this meniscus through a low-power microscope with an ocular micrometer, very slight movements may be observed and measured. It is easy to construct the instrument so that an electromotive force of one-thousandth of a volt produces a movement of three or four scale divisions. It is thus an admirable " zero " instrument. Moreover, through a narrow range the movement is proportional to the electromotive force, and so we may estimate to less than a ten-thousandth of a volt from its behavior. But no large electromotive force should be applied, for the surface at C is sensitive. If, the minus electricity entering at B, the electromotive force exceeds one volt, or if, plus electricity entering at B, the electromotive force exceeds two or three one-hundredths of a volt, the surface will be damaged through electrolysis. If this should happen, by blowing in at B a drop of mercury may be forced out of the capillary (falling into A) and so a new surface may be secured.*

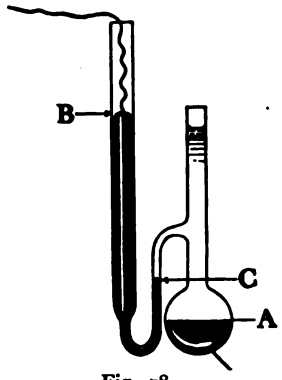


Fig. 78.

The Double-layer Theory. With a slightly different form of the instrument (but the form just described would do equally well) Lippmann determined the extent of the movements as he applied higher and higher potentials of minus electricity at the meniscus in the capillary. He plotted these paired values against each other, the

* The surface remains in good order only if the instrument is kept short-circuited, except for the second or so at a time while a measurement is being made. A key in the circuit takes care of this automatically. For additional details as to its construction and use see the laboratory manuals cited at the beginning of Chapter XXVIII.

movements on the vertical, the potentials on the horizontal. The curve thus obtained showed a maximum height at about 0.8 volt. This, then, is the potential we must apply to neutralize the potential which is produced by the contact of dilute sulphuric acid with a mercury surface. One must then equal the other.

Helmholtz likened the conditions at the surface of contact between the mercury and the sulphuric acid to a charged condenser. The mercury surface is charged plus, and very near to it there must be a layer of ions charged minus. The capacity of a condenser with parallel plates and a given difference of potential is inversely proportional to the distance apart of the plates. Applying these facts, he calculated the distance between the charge on the mercury surface and the " shell of ions " about it to be about 0.4 to 0.8×10^{-7} cm. *i.e.*, of the order of molecular dimensions. It is not easy to understand how such a " double layer " is produced. The suggestion has been made that the cleanest mercury surface carries traces of oxide, or else oxide is formed at once upon contact with the electrolyte. This oxide may dissolve as ions with minus charges, leaving the mercury charged plus. This may or may not seem to be a satisfactory explanation, but the fact remains that the mercury is charged plus. This charge is a satisfactory explanation of the behavior of the mercury. Surface tension may be considered as the result of the mutual attraction of molecules in the surface. If these molecules are charged with electricity of the same kind, these charges repel each other, work against surface tension, and so diminish it.

We shall have occasion to refer again to Lippmann's work and Helmholtz's double-layer theory in connection with the measurement of single potentials. But having now described enough laboratory facts to show how we can determine the electromotive force of a source, it seems best to consider some of those sources. The most important source is, of course, the dynamo; but this is purely physical, with no chemical feature about it, and so its consideration falls wholly without the scope of this book. We shall confine our attention to those combinations wherein chemical energy is converted to electrical, and the converse, *i.e.*, to " batteries " or " cells."

Primary and Secondary Batteries. These cells are classified as primary if, without previous action of electrical energy, they will furnish a current, and as secondary if they require that a current shall be sent into them before they are in condition to deliver a current. The more usual, and better, name for the second sort is

"storage batteries." We shall begin with a consideration of primary batteries, sometimes called "voltaic cells" or "galvanic cells," sometimes called "elements."

In General upon "Cells." From what has been said in the earlier portion of this chapter we have learned that wherever there is a surface separating two phases this surface may be a source of electrical potential. About the simplest cell conceivable consists of two electrodes immersed in a solution in which one dissolves. Typical is the Leclanché element, consisting of a rod of zinc and a rod of carbon, both immersed in a solution of ammonium chloride. We have here two sources of potential, — the contact between the zinc and the solution, and the contact between the carbon and the solution. The electromotive force of such a combination is of course the algebraic sum of all the sources.

A little more complex is a cell consisting of two electrodes, one in one solution, one in another, the solutions in contact and one electrode dissolving. Typical of this class is the Daniell element, which consists of zinc in a zinc-sulphate solution within a porous cup, and copper in a copper-sulphate solution without. The specific gravity of the zinc-sulphate solution is the greater and diffusion is very slow. Owing to the part played by the attraction of gravitation, this is sometimes called a "gravity battery." Instead of depending upon the difference in specific gravities, the solutions are often separated by a porous porcelain cup (jar or cell). These arrangements are identical so far as the reasoning goes. In this cell we have three sources of potential, — the contact between the zinc and its solution, the contact between copper and its solution, and the contact between the two solutions.

There is a third type, called a "concentration cell." We may have two electrodes of the same material, both immersed in a solution of one substance. But the first electrode is immersed in a solution of concentration C_1, and the second in a solution of different concentration, C_2. This cell also has three sources of potential, — the contact between each electrode and its solution, and the contact between the solutions.*

Reversible and Nonreversible Cells. There is another classification of cells which to a certain extent overlaps the classification

* For the many other combinations which have proved to be of value and interest as sources of potential, the reader is referred to more highly specialized works.

just given. We subdivide cells into those which are reversible and those which are nonreversible. By a reversible cell, we mean one in which, by sending the current into the cell, we may accomplish the exact reverse of the chemical process which takes place when the cell itself is furnishing the current. Typical of this class are the Daniell cell and the ordinary lead storage battery.

The Daniell cell is thus "typical" of two classes, both primary and secondary cells, and we have here an admirable illustration of the futility of supposing that any of our artificial classifications are final.

In nonreversible cells we cannot reverse the chemical process by sending a current through the cell. When we try to do so electrolysis occurs; for example, water is electrolyzed and a gas (or gases) is given off. The Leclanché cell may be considered as a typical nonreversible cell.

A convenient way to represent cells is by writing the formulæ of the essential chemical substances one after the other, indicating the sources of potential by dashes. For instance, the Leclanché cell is definitely indicated by the combination, Zn–NH_4Cl solution–C; the Daniell cell by Zn–$ZnSO_4$ solution–$CuSO_4$ solution–Cu.

Osmotic Theory as to Production of Potential. As an introduction to the osmotic theory of the production of the potential differences which we observe in cells, and which we owe in its present form to W. Nernst, it will be well to repeat a few facts stated in previous chapters. Every substance has a definite tendency to go into solution. We call this its solution pressure, and it is analogous to vapor pressure. Every substance has a tendency to come out of solution. We may call this its precipitation pressure, and Nernst assumes that its osmotic pressure is a measure of this. We assume that a salt dissolves as such in the first instance, and then (practically instantaneously) dissociates to a definite degree to equally and oppositely charged anions and cations. This cannot produce a potential measurable by our present methods. But when metals dissolve they can send only cations, plus charged ions, into the solution; consequently the metal which remains behind must become charged with an equivalent quantity of minus electricity. The minus charged metal must attract the plus charged ions to such an extent that some ions redeposit themselves; but other ions must be going into solution continuously, and so we have a condition of equilibrium in almost all particulars like those we consid-

ered in Chapter XXVI. The metal appears not to dissolve, but we imagine that it is dissolving and precipitating at the same rate. At the surface of contact, then, there is a " double layer," which has a tension measured as a difference in electrical potential. This difference of electrical potential must, then, be proportional to, and measurable by, and so must be itself a measure of, the pressure of solution. If we close the circuit outside, that is, give these charges another path by which they can get to each other, this " double-layer " equilibrium is upset and more metal dissolves. This dissolving continues until the osmotic pressure of the ions (precipitation pressure), unaided by any electrical attraction, equals the solution pressure, when, again, we have an equilibrium. Such, in brief, is Nernst's theory, the utility of which will be apparent from what follows.

Formula for the Potential at a Metal Electrode. We shall first apply it to the calculation of the potential at a metallic electrode in contact with a solution of a salt of that metal. Call the solution pressure of the metal P and the osmotic pressure of the ions in solution p. The metal that dissolves goes from pressure P to pressure p, and we shall consider that this is the same as if metal ions at an osmotic pressure P expanded to an osmotic pressure p. Van't Hoff has shown that the gas laws hold for substances in solution when we substitute osmotic pressure for gaseous pressure in the formula $pv = RT$, so the effect is the same as if a gas expanded from P to p.

We learned in Chapter XXII that when a formula weight in grams of any gas expands isothermally from an original pressure p_1 to a final pressure p_2, the maximum amount of work we can obtain (A) is given by the formula $A = RT\ln \frac{p_1}{p_2}$. The maximum work obtainable when a gram molecule of a metal with solution pressure P goes into solution isothermally and becomes ions at an osmotic pressure p is, then, $A = RT\ln \frac{P}{p}$.

Consider an univalent metal and that one equivalent weight in grams goes into solution. The ions resulting will then carry a quantity of electricity equal to Faraday's constant, 96 500 coulombs. Let F represent this quantity. But the total electrical energy is the quantity times intensity, or coulombs times volts, or $F\pi$, where π represents the potential. If all work is converted without loss to electrical energy, $F\pi$ must equal $RT\ln \frac{P}{p}$, or $\pi = \frac{RT}{F} \ln \frac{P}{p}$.

In case the metal is not univalent but has the valence, n, the quantity of electricity associated with the ionization of a gram atom is nF, and so our formula becomes $\pi = \frac{RT}{nF} ln \frac{P}{p}$.

If a cell is reversible, this means that whatever amount of electrical energy we put in is converted to chemical energy, and, reversing, we can get the same amount back without loss. The transformations both ways must then be complete and without loss in other forms of energy. A strictly reversible cell fulfills, then, the above requirement, and the equation just given is fundamental for all reversible cells.

From the gas laws we know $R = \frac{pv}{T}$. Adopting standard or normal conditions, $p = 1$ atmosphere (760 mm.) = 1033.3 g. cm.; $v = 22\,400$ cm^3; $T = 273$. To convert to the C. G. S. system we must multiply by the gravitation constant, 981, so we have

$$R = \frac{22\,400 \times 1033.3 \times 981}{273} \text{ ergs.}$$

Natural logarithms are converted to ordinary Briggs logarithms (basis = 10) by the formula $ln x = 2.3026 \log x$. $F = 96\,500$. Unit electrical energy, one joule, as explained in Chapter XXVIII, is 10^7 ergs. Substituting in the formula, we have

$$\pi = \frac{22\,400 \times 1033.3 \times 981 \times 2.3026}{273 \times 10^7 \times 96\,500} \frac{T}{n} \log \frac{P}{p} \text{ or } \pi = 0.000\,198\,3 \frac{T}{n} \log \frac{P}{p} \text{ volts.}$$

Suppose we are working at an average room temperature of 18°; then $T = 291$, and we have $\pi = \frac{0.057\,69}{n} \log \frac{P}{p}$ volts.

Formula for the Potential at Contact of Two Solutions. Nernst's osmotic theory is the first plausible explanation for the long-known fact that there is a potential difference at the surface of contact between two solutions.

Imagine two solutions of hydrochloric acid of different concentrations in contact. The solute will diffuse from the place where it is more concentrated to the place where it is less concentrated. But, according to the dissociation theory, hydrogen cations and chloride anions are independent individuals, and so will tend to diffuse at different rates. The hydrogen cations, being the lighter, will tend to move the faster. Presently the " front rank " will consist of hydro-

gen cations charged plus, while behind them will be an excess of chloride ions charged minus. Thus a difference of potential may be established. Electromagnetic attraction between opposite charges prevents them from getting apart, but we can easily visualize how a layer of plus charges will be toward the more dilute solution, and a layer of minus charges toward the more concentrated solution of the acid.

Thus the unequal rates of migration of the ions are the cause of the potential difference. If the negative ion travels faster, of course the more dilute solution will show a minus charge. The more dilute solution always is charged with electricity of the sign of the faster ion.

Suppose we have the same electrolyte at two concentrations, that it consists of two univalent ions, and that U is the transference number for the cation and V the transference number for the anion, as defined in the last chapter. Suppose, also, that the cation moves faster than the anion. Consider that unit quantity of electricity (96 500 coulombs) is carried from the concentrated to the dilute region. The total conduction is then $U+V$, and $\frac{U}{U+V}$ cations must have gone one way, while $\frac{V}{U+V}$ anions must have gone the other.

Let p equal the osmotic pressure of the cations in the concentrated solution; it must then also be the osmotic pressure of the anions in the same solution. Let p_1 equal the osmotic pressure of the cations (and of the anions) in the dilute solution.

We have just seen that the maximum work we can get when a formula weight of ions expand from the higher pressure p to the lower pressure p_1 is $RT\ln\frac{p}{p_1}$. If all the work is converted to electrical energy, the movement of the cations will then give us $\frac{U}{U+V}RT\ln\frac{p}{p_1}$. The anions move in the opposite direction, from the region of less to that of greater pressure. They therefore require work to be done upon them equal to $\frac{V}{U+V}RT\ln\frac{p}{p_1}$. Hence we may expect to obtain as electrical energy only the difference between these two quantities, or $\frac{U}{U+V}RT\ln\frac{p}{p_1}-\frac{V}{U+V}RT\ln\frac{p}{p_1}$. Simplifying, $\frac{U-V}{U+V}RT\ln\frac{p}{p_1}=F\pi$.

Substituting numerical values for symbols as we did in deriving the equation for the potential at an electrode, we have

$$\pi = \frac{U-V}{U+V} 0.057\,69 \log \frac{p}{p_1},$$

an equation giving the potential at the contact between two concentrations of an electrolyte consisting of two univalent ions.

A Concentration Cell. We are now in a position to consider a concentration cell as a whole. Suppose we have two silver electrodes, one dipping in $\frac{n}{10}$ $AgNO_3$, the other dipping in $\frac{n}{100}$ $AgNO_3$. Let P equal the solution pressure of the silver, p_1 the osmotic pressure of the ions in $\frac{n}{10}$ $AgNO_3$, and p_2 the osmotic pressure of the ions in the $\frac{n}{100}$ $AgNO_3$. At the first electrode we have $RTln\frac{P}{p_1}$; at the contact between the two solutions we have $\frac{U-V}{U+V} RTln\frac{p_1}{p_2}$; at the second electrode we have $RTln\frac{P}{p_2}$, and this is opposed in its effect to the first electrode. Therefore we place a minus sign before it and then add the three terms to obtain the electromotive force of the cell as a whole. Adding and simplifying, we obtain, $-\frac{2V}{U+V} RTln\frac{p_1}{p_2} = F\pi$, or

$$-\frac{2V}{U+V} 0.057\,69 \log \frac{p_1}{p_2} = \pi.$$

Referring to the table in the previous chapter, we find U for $Ag^{\cdot} = 51$ and V for $NO_3' = 57$. If the silver nitrate were completely dissociated in both solutions, the osmotic pressures of the ions would be as 10 is to 1, $\frac{p_1}{p_2}$ would equal 10, and $\log 10 = 1$. But conductivity measurements prove that the dissociation is not complete, that the ratio between the concentrations of the ions in the two solutions is as 8.71 is to 1. Therefore $\frac{p_1}{p_2} = 8.71$. Substituting these values, we have $\pi = -\frac{114}{108} 0.057\,69 \log 8.71$, or $\pi = 0.0572$. By actual experiment this cell was found to have an e.m.f. of 0.055 volt. The agreement between fact and theory is all one could ask.

In General Regarding Concentrations. If the concentrations of the ions in the two solutions are as 100 : 1, we have log 100, which is 2; if the concentrations are as 1000 : 1, we have log 1000, which is 3, as a factor to insert in our equation. Thus we see that very great changes in the concentrations of the solutions make relatively much smaller changes in the e.m.f. of a concentration cell.

Suppose a metal were immersed in a solution containing none of that metal as ions. We should have $ln\frac{P}{o}$, but that is infinity, and so the e.m.f. of the cell should be infinitely great. This is never the case, however, and so we must assume that every metal sends some ions into every solution at once. We here have another argument for our belief that nothing is absolutely insoluble.

Amalgam Electrodes. It is possible to alter the solution pressure of a metal by using as electrodes amalgams of the metal at different concentrations. The development of an equation for such a cell is quite similar to what has just been given. For details the reader is referred to texts on electrochemistry. It must suffice to say that there is an admirable agreement between fact and theory.

Gas Electrodes. Platinized platinum absorbs large quantities of gases. We may construct cells having electrodes consisting of strips of platinized platinum immersed, half in the solution, half in the gas. Such cells behave as if the electrodes consisted solely of the gases used. Interesting as these combinations are, it is necessary once more to refer the reader to more specialized books for details.

Measurement of Single Potentials. A complete cell consists, necessarily, of at least two, and often more, sources of potential, and when we measure the e.m.f. of the cell we determine the algebraic sum of all the sources. It is a matter of interest to learn how much is due to each source; to measure single potentials. We cannot do this by measuring a complete cell, for we have at least two unknowns, and such equations are indeterminate. If we can determine one single potential, we can solve all our equations. But therein lies the difficulty, — to settle definitely some one, as a starting point. A number of expedients have been tried, but it cannot be said that any one has definitely solved the problem.

According to Helmholtz's " double layer " theory the surface tension between two liquids reaches a maximum when the potential difference between them is zero. We may then construct a Lippmann capillary electrometer with solutions of different electrolytes and de-

termine the potential which must be applied to give the mercury its maximum surface tension, in the way described earlier in this chapter. This must then be the potential between the mercury and the electrolyte. Suppose that we do this with electrolytes A and B. Now set up a cell according to the scheme Hg–A–B–Hg and measure its e.m.f. Since the e.m.f. of a cell is the algebraic sum of all the sources, if we know the single potentials Hg–A and Hg–B, it is easy to calculate the potential A–B.

But there are many serious difficulties in practice. For instance, it is hard to determine just when the mercury has its maximum surface tension, for in this region fairly large differences in the potential impressed make relatively small changes in the surface tension. We can probably say that the potential between a mercury surface and equivalent normal sulphuric acid is not less than 0.8 and not more than 0.9 volt. But such an approximation is not in the least satisfactory as a standard of reference where we wish to express our results to a thousandth of a volt or less.

A " dropping electrode," a capillary orifice out of which come so many fine, separate particles of mercury as to constitute a " mist," to fall into a larger body of mercury beneath, should have zero potential according to Helmholtz, and was considered as the sought-for standard for some years. But Nernst has raised a number of valid objections, and it is not now sufficiently generally accepted to require a careful description.

Nernst has suggested that, since the main interest lies in the comparative values, we arbitrarily adopt a point of departure until future investigations give us something better. He further suggested that a hydrogen electrode, platinized platinum half in hydrogen gas and half in a solution of sulphuric acid of such concentration that it contains one gram of hydrogen ions per liter, being in fact near the zero point, be adopted as exactly zero. A current of hydrogen gas must be kept bubbling through the solution, and other precautions must be observed. The experimental manipulation of this " zero " electrode is not exactly easy. We have, therefore, devised what we call a " normal " electrode, easily reproduced, and with a definite potential most carefully compared with this hydrogen electrode.

Normal Electrode. Formerly the normal electrode consisted of amalgamated zinc in a saturated solution of zinc sulphate, but preferable to this is the so-called " calomel " electrode.

Calomel Electrode. Fig. 79 is a sketch of the "calomel" electrode, approximately half the customary size. A small jar, about 8 cm. high and 3 cm. in diameter, contains a few cm.^{3} of pure mercury at the bottom. Above this is a layer of mercurous chloride, rubbed up to a paste with a normal solution of potassium chloride. The rest of the jar is completely filled with this solution, which also fills the glass and rubber tubes marked *A*, *A*, *A*, in the figure. Electrical connection with the mercury at the bottom is established by means of a wire sealed through the closed glass tube indicated at *B*.

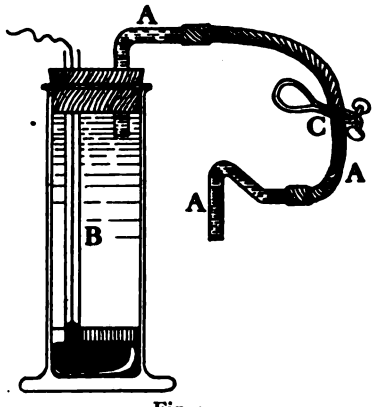


Fig. 79.

This affair is only half a cell, but if the bent tube, *A*, is dipped beneath the surface of a second electrolyte containing a second electrode in another jar, and the pinchcock *C* is opened, we have a complete cell whose e.m.f. we can measure. We have, then, really three sources of electromotive force: first, the normal electrode; second, the contact betweeen the two electrolytes; third, the other electrode. We chose potassium chloride for our normal electrode because its two ions travel with nearly the same velocity and so set up a minimum potential difference at a contact with another solution. This almost surely does not hold for the other solute however, and so there is always a potential difference at this contact. It is customary to ignore this, and, subtracting the value for the calomel electrode from the measured e.m.f., to say that the difference is the potential between the second electrode and its solution.

Potential of the Calomel Electrode. When a cell is made up consisting of a calomel electrode and a hydrogen electrode, it is found to have an e.m.f. of 0.283 volt, the plus current traveling, in the cell, to the mercury electrode. Having decided to call the potential of the hydrogen electrode zero, we then say the potential of our calomel electrode is +0.283 volt, indicating by the + sign that the metallic electrode is charged in that sense. Some writers put the potential of the calomel electrode equal to zero. While this does not alter the relative position of anything, it makes the recorded values yet further from the true values, and this seems unnecessary.

Temperature Coefficient of the Calomel Electrode. The temperature coefficient of the calomel electrode is but 0.000 07 volt per degree; in other words, entirely negligible in all but the most refined of measurements. This is a distinct advantage.

Some Observed Values. From what has been said it will be realized that the potential between a metal electrode and a solution of one of its salts is independent of the anion, but depends on the concentration of the cation. Thus the same potential will be obtained if we use the chloride, nitrate, or sulphate, provided we use them in such concentrations that the concentrations of the cations are the same. The following table contains a few of the values obtained by Wilsmore* for the metals indicated, immersed in solutions of salts of the same metal of such concentration that they contain an equivalent weight in grams of the metal as ions per liter. In all cases the values represent actual experiment, but in most cases the concentration of the cations was not equivalent normal and a calculation was necessary to reduce the experimental value to that standard. The hydrogen electrode was adopted as the point of reference and set equal to 0. To quote Wilsmore: "In no case is the third decimal place to be considered as certain, and in the majority of cases perhaps the second decimal place is uncertain."

Al	Mn	Zn	Cd	Fe	Co
−1.276?	−1.075	−0.770	−0.420	−0.340	−0.232
Ni	Sn	Pb	Cu	Hg	Ag
−0.228	<−0.192	−0.148	+0.329	+0.750	+0.771
Pt	Au	Cl	Br	I	O
<+0.863	<+1.079	+1.417	+0.993	+0.520	+1.119?

The value of such a table is very great, for it enables us to foretell what the e.m.f. would be of any cell we might construct. For instance, suppose we make up a cell consisting of a zinc electrode in a solution containing an equivalent weight in grams of $Zn^{\cdot\cdot}$ and a copper electrode in a solution containing an equivalent weight in grams of $Cu^{\cdot\cdot}$. The table tells us the zinc will charge itself minus to the extent of 0.770 volt and the copper will charge itself plus to the extent of 0.329 volt. These two charges will evidently be "pushing" the same way so far as sending a current through an outside circuit is concerned, so the e.m.f. of the combination will be 0.770 + 0.329 = 1.099 volts. This is the Daniell cell and its e.m.f. is 1.096 volts, a fairly good check.

* N. T. M. Wilsmore, *Zeitschr. f. phys. Chem.*, **35**, 291–332 (1900).

If the concentration of the ions is less than assumed above, this will have the tendency to make the metal electrode more negative or less positive. This is a corollary of what has been said regarding the solution pressure.

Potential Series. The table gives us what we call an electrochemical, or better, potential, series of the elements. It is rather significant. Thermochemical data give us measures of total chemical energy but tell us next to nothing regarding the individual factors, as was explained in Chapter XXVII. The single potential, however, seems to be a measure of the intensity factor, that factor which determines whether or not a given process will take place. It seems as though we could say that the intensity factor of the chemical energy possessed by an element is the greater, the higher it stands in this series. This view has cogent arguments in its favor. Any metal in the series, brought in contact with a solution of a salt of a metal standing below it, will dissolve, displacing this "lower" metal from its salt, forcing, as we might say, this "lower" metal to deposit as such. For instance, zinc put in a solution of a copper salt will dissolve, and copper will precipitate. Any metal standing "above" hydrogen in this series will displace hydrogen from its "salts," the acids; that is, will dissolve in acids with the evolution of hydrogen. Those standing "below" hydrogen will not do this.

The practical application of these simple principles are numerous and important. Unfortunately we cannot, in this brief summary, more than indicate what they are. "Galvanized" iron is sheet iron covered with a thin layer of zinc. If this layer is scratched or worn in such a way as to expose the iron, and moisture collects at the spot, we have a "short-circuited" cell. The zinc dissolves more rapidly than if the iron were not there. "Tinware" is iron coated with tin. If the tin coat is removed at some spot the iron rusts faster than if it were not tinned. The corrosion of underground gas and water pipes has taken place to a serious extent since the general introduction of trolley cars. It diminishes the troubles if the "plus" terminal of the dynamo is attached to the overhead wires. Then the "return wire," consisting of the rails, and inevitably of at least sections of gas and water pipe, becomes the cathode in this magnified cell, and suffers less damage, for metals deposit on the cathode.*

* Do not suppose that this is a final solution of this vexatious problem; it is given solely as an indication of how a familiarity with, and ability to apply, fundamental principles may be of "practical" value.

Oxidation and Reduction Series. The electromotive series of the metals is also the series of their oxidizability, and may be considered as the order of their "affinity" toward oxygen. We may carry this idea further. Some substances in solution act as oxidizing agents, others as reducing agents. We can arrange them in the order of their tendency to oxidize or reduce, and so obtain an oxidation and reduction series.

Before we go further in this discussion it will be well to define what we mean by oxidation and reduction in the light of electrochemical phenomena. The terms have been extended until they include processes in which oxygen takes no part. If a strip of copper is put in a solution containing silver ions, silver is precipitated and copper dissolves. We say the silver has been reduced and the copper oxidized. We believe that silver ions were deprived of plus charges and copper ions received them. When the stannous ion $Sn^{\cdot\cdot}$ is converted to the stannic ion, $Sn^{\cdot\cdot\cdot\cdot}$, we say it has been oxidized. When the ferric ion, $Fe^{\cdot\cdot\cdot}$ is deprived of one unit charge and becomes the ferrous ion, $Fe^{\cdot\cdot}$, we say it has been reduced. So oxidation as at present understood means the addition of plus charges or the subtraction of minus charges; reduction means the subtraction of plus charges or the addition of minus charges; and oxygen may not enter into the process at all. In the terms of the electron theory oxidation consists in the removal, reduction in the addition, of electrons.

Bancroft and others have investigated many combinations, constructing cells with two platinum electrodes immersed in different solutions. As the platinum was never attacked, the electromotive forces of these cells were to be considered as additively made up of the tendencies of the ions in the two electrolytes to give up or acquire charges of one sign or the other.*

The following table contains an oxidation and reduction series as found by Bancroft. The substances were investigated at a concentration of one-fifth normal wherever possible. The minus sign may be taken as indicating that the substance is a reducing agent; the plus sign then indicates that the substance is an oxidizing agent. The numbers themselves represent single potentials expressed in volts, and may be thought of as measures of the intensity factors of the chemical energy of the several substances. The table then contains measures of the relative "strengths" of oxidizing and reducing

* W. D. Bancroft, *Zeitschr. f. phys. Chem.*, 10, 387–409 (1892); B. Neumann, *Zeitschr. f. phys. Chem.*, 14, 193–230 (1894).

agents. It should be remembered that the values are not absolute but merely relative.*

OXIDATION, REDUCTION SERIES.

Stannous chloride in alkaline solution	−0.861
Sodium sulphide	−0.651
Hydroxylamine in alkaline solution	−0.616
Pyrogallol in alkaline solution	−0.482
Hydrochinone in alkaline solution	−0.329
Hydrogen in acid solution	−0.311
Potassium ferrocyanide in alkaline solution	−0.086
Stannous chloride in acid solution	−0.064
Cupric chloride	+0.000
Sodium thiosulphate	+0.016
Sodium sulphite	+0.023
Ferrous sulphate in neutral solution	+0.073
Hydroxylamine in acid solution	+0.076
Sodium hydrogen sulphite	+0.103
Sulphurous acid	+0.158
Ferrous sulphate in acid solution	+0.234
Iodine in KI solution	+0.328
Potassium dichromate	+0.502
Ferric chloride	+0.678
Nitric acid	+0.697
Bromine in alkaline solution	+0.755
Chromic acid	+0.837
Potassium iodate	+0.929
Chlorine in acid solution	+1.106
Potassium permanganate	+1.203

Polarization. Suppose that we have electrodes of some material not attacked by the electrolyte, as for instance of platinum, gold, or carbon, and that we send a current through such a cell under a constant electromotive force. The current gradually diminishes. There develops, as it were, an opposing electromotive force at the electrodes, which resists the effort to send the current through. This

* The numerical values are not those given by Bancroft, but are taken from Le Blanc's "Electrochemistry," translated by Whitney, to which text those desiring additional details are referred. Though the numbers are different, the relations are maintained. For instance, in this table the tendency to reduce possessed by an alkaline solution of $SnCl_2$ is represented by 0.861 volt, the tendency to oxidize possessed by a solution of $KMnO_4$ is represented by 1.203 volts. The difference between these intensity factors is their sum, or 2.064 volts. Bancroft and Neumann represent the $SnCl_2$ value with +0.301 and the $KMnO_4$ value with −1.763. The total difference is the sum, or 2.064, the same value. In other words, the pictures are the same, only displaced along an arbitrary scale.

phenomenon is called polarization. If the current is stopped, such polarized electrodes are able to send a current in the reverse direction for a time. Our present theory is that ions are piled up about a polarized electrode and are striving to go back and distribute themselves evenly through the solution.

Measurement of Polarization. Fig. 80 represents a combination of instruments to measure polarization. *A* is the cell undergoing polarization, *B* the battery or other source of current producing the polarization, *C* is a capillary electrometer or other sensitive current detector, and *D* is a source of potential which may be varied at will; a potentiometer. *E* is one arm of a tuning fork, connected to one electrode of *A* but vibrating in such a way as to make contacts in rapid succession at *F* and *G*. When the contact is made at *F*, a current from *B* flows through *A* and polarizes the electrodes. When the contact is made at *G*, this "back electromotive force" due to polarization sends a current through *D* and *C*. *D* is now varied until *C* shows no current passing, and then the known potential of *D* is said to be the electromotive force of the polarization.

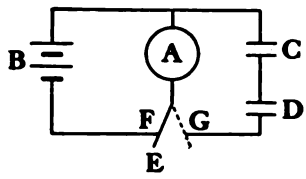


Fig. 80.

Measurement of Polarization at One Electrode. Fig. 81 illustrates the method of measuring the polarization at one electrode. Into one and the same electrolyte dip the two electrodes *A* and *B* and the siphon of the normal electrode *C*. *D* is the source which polarizes *A* and *B*. *E* is an electrometer and *F* a variable potential.

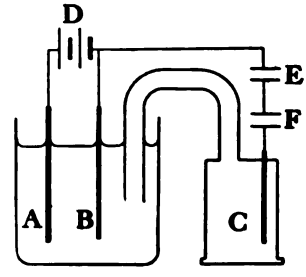


Fig. 81.

Before sending a current from *D* through *A* and *B*, we measure the e.m.f. of the cell consisting of *B* and *C*. We next send a current from *D* through *A* and *B*, so polarizing *B*. We then measure again the e.m.f. of the cell *B*, *C*. The difference between this value and the value obtained before the polarizing current from *D* was sent in must be the measure of the polarization of *B*. We can transfer the connection from *E*, shown in the figure as attached to *B*, to *A*, and measure its polarization in like manner.

Decomposition Potentials. Suppose we have two indifferent electrodes in an electrolyte and apply a low potential. A galva-

nometer in the circuit shows a wide deflection when the contact is made, but rapidly comes back nearly, but not quite, to its zero point. This shows that the polarization in the cell has become nearly, but not quite, equal to the impressed e.m.f. Repeat, increasing this impressed e.m.f. a little each time. We shall thus be able to find a minimum e.m.f. at which the deflection of the galvanometer is large and remains large, not sinking nearly to zero. The point so determined is rather definite. If impressed e.m.f. is laid off on the abscissa against galvanometer deflections on the ordinate, the curve so obtained shows a decided upward slant at the point in question.

We believe that a current is transported through a solution solely by the ions, and that polarization consists in a banking up of the ions at the electrodes. Then the minimum e.m.f. at which the galvanometer shows a constant current flowing through the cell must be the e.m.f. required to force the ions to deposit their charges on the electrodes and become electrically neutral substances. It must, in short, be the lowest potential adequate to produce electrolysis. This is a characteristic quantity for different electrolytes, and, for obvious reasons, is called the decomposition potential.

The following table gives a few of the decomposition values, in volts, for the electrolytes named, all in normal solution, as determined by Le Blanc.*

$ZnSO_4$	2.35	HNO_3	1.69
$ZnBr_2$	1.80	H_3PO_4	1.70
$NiSO_4$	2.09	HCl	1.31
$NiCl_2$	1.85	NaOH	1.69
$Pb(NO_3)_2$	1.52	KOH	1.67
$AgNO_3$	0.70	NH_4OH	1.74
H_2SO_4	1.67		

The decomposition value is practically the same for all acids and bases. This is because, when we electrolyze solutions of these substances, we always get the same results; hydrogen is given off at the cathode and oxygen at the anode. So we are really measuring the decomposition value of water. Some acids give a different value, as HCl in the above table. But when we electrolyze this, chlorine is obtained at the anode, so we are not electrolyzing water.

These values are dependent upon the nature of the electrode. For example, the decomposition voltage of 1.67 for water, as shown in

* *Zeitschr. f. phys. Chem.*, 8, 299–330 (1891).

the above table, was obtained with plain platinum electrodes. If platinized platinum electrodes are used the decomposition voltage is 1.22. Other metals will give other values. Moreover, the decomposition voltage is dependent upon the partial pressure of the gases at the electrodes, becoming less the lower this pressure, as is evident from the formulations we have developed. This maximum value of 1.67 volts corresponds to a pressure of one atmosphere on both hydrogen and oxygen. If the partial pressures are nearly zero, nearly zero potential will electrolyze minute quantities of water. Of course much cannot be so electrolyzed without raising the gaseous pressures. This will account for the small " residual current " proved to be present by the fact that the galvanometer does not come all the way back to zero, though the e.m.f. impressed is much below the decomposition value, and though we wait hours or even days.

Intensity of Fixation of the Ions. The decomposition value is the sum of two quantities, — the potential required to force the cations to give up their charges and become electrically neutral substances, plus the potential required to force the anions to do likewise. If we knew this potential for one single kind of ion, we could at once determine it for each and all other kinds of ions. But we do not. We arbitrarily assume that it requires zero potential to force hydrogen ions to give up their charges and become electrically neutral molecules, and with this as a starting point have constructed tables which give what we call the intensity of fixation of individual kinds of ions. The following table gives the intensities of fixation of the ions named, in solutions containing " normal " concentrations of these ions.*

Mn	+1.075	Hg	−0.748
Zn	+0.770	Ag	−0.789
Cd	+0.421	I	−0.520
Fe	+0.343	Br	−0.993
Tl	+0.322	O	−1.23
Co	+0.232	Cl	−1.353
Ni	+0.228	OH	−1.68
Pb	+0.136	SO_4	−1.9
H	±0.000	HSO_4	−2.6
Cu	−0.336		

The + sign may be considered as indicating a tendency to go into solution. So, zinc having the value +0.770, we must apply 0.770

* Taken from N. T. M. Wilsmore, *Zeitschr. f. phys. Chem.*, 35, 291–332 (1900). The values for the anions, beginning with iodine, are taken from Nernst, sixth edition, p. 750.

volt more than the potential of hydrogen to cause zinc to precipitate. The − sign may be taken as indicating a tendency to come out of solution, and so, copper having the value −0.336, may be supposed to require no external potential to cause its deposition. It would deposit of itself if not held back by the other oppositely charged ions.

From these values we can, of course, by simple summation, obtain the decomposition values, *i.e.*, the e.m.f. required to electrolyze a solution containing these ions at normal concentration. For example, the e.m.f. required to electrolyze zinc bromide is 0.770 + 0.993, or 1.763 volts; the e.m.f. required to electrolyze hydrochloric acid in which the ions are at normal concentration is 1.353 volts, etc.

We can also use these values to calculate the e.m.f. of a cell. For instance, in the Daniell cell we have Zn dissolving in $ZnSO_4$ solution and Cu coming out of a $CuSO_4$ solution. If the ions in these solutions are at normal concentration, we shall have an e.m.f. of 0.770 + 0.336 = 1.106 volts.

There is another interesting point in this connection. For silver iodide we have the value 0.520 − 0.789 = −0.269. That is, we do not need to apply a potential to this salt; it will separate of itself, and give an electromotive force of 0.269 in so doing. That is, it would do this if we had it in normal concentration of the ions. But it is exceedingly insoluble, and such a concentration is quite impossible. It is probable that this tendency to separate and come out of solution is closely allied with the solubility of the substance. But it must be acknowledged that the facts are often not in accord with the deductions made from this premise.

Application of These Principles to Analysis. The study of these relations is of importance in electrochemical analysis. It is usual to lay much stress on the current density, which is indeed important as determining the condition of the deposit, whether coherent and weighable, or pulverulent, readily detached from the electrode, and not weighable. But more important even than this is the judicious regulation of the electromotive force.

Suppose we have a solution containing both copper and cadmium. Apply an e.m.f. greater than necessary to drive out the copper but not great enough to deposit cadmium. The copper will precipitate quantitatively and when it has all come out the current will almost cease to pass. We may take the electrode out and weigh it, thus determining the copper, then replace it, increase the e.m.f., and precipitate the cadmium quantitatively. Of course as the concentration of

the copper becomes less the potential required to drive it out becomes greater. But remember that the potential at an electrode, $\pi, = \frac{RT}{nF} ln \frac{P}{p}$. It is evident that great diminution in the concentration of the ion, measured by p, involves a relatively small increase in the potential, π, which must be overcome.

The difference in intensity of fixation of metallic ions is large enough to permit us to apply this scheme of separation in many cases. The principle is at the basis of the commercial refining of copper. Masses of the crude copper are cast and made the anodes. Thin sheets of pure copper are used as cathodes and a low e.m.f. is applied. Silver, gold, and platinum do not dissolve, but fall as a sort of mud, from which they may be recovered. Zinc and iron go into solution, but remain there, because the e.m.f. is not allowed to become large enough to precipitate them.

Illustration of the Value of Theories. Ordinarily copper is in solution as $CuSO_4$. The ion is bivalent and requires $2 \times 96\,500$ coulombs to precipitate 63.6 grams. In Höpfner's method * a solution of ferric chloride and common salt is used as the electrolyte and the copper dissolves as cuprous chloride. This copper ion is univalent and requires only 96 500 coulombs to precipitate 63.6 grams.

Relation between Chemical Energy and Electrical Energy. We can measure chemical energy in terms of heats of reaction. One calorie equals 42 660 g.-cm., or 4.183×10^7 ergs. The unit of electrical energy is the volt-coulomb, or joule, and this is equal to 10^7 ergs. Thus one calorie = 4.183 j. The heat of reaction, H, is the number of calories evolved or absorbed when a formula weight of the substance reacts. Let n equal the valence of the reacting substance, that is, the number of chemical unit quantities involved. In any electrolytic process the change of one chemical unit quantity is accompanied by the transference of 96 500 coulombs (one Faraday, denoted by F). Then, if in any process the chemical energy is converted without loss to electrical, $\pi F = 4.183 \frac{H}{n}$, where π is the e.m.f. in volts.

How complete the conversion actually is in any given cell may be determined with ease. Send the current through a long fine wire immersed in a calorimeter, and determine the heating effect in calo-

* *Zeitschr. f. Angewendte Chemie*, 1891, p. 160. A good description may be found in "Practical Electro-Chemistry" by B. Blount, pp. 76–86. The process is not a commercial success owing to serious mechanical difficulties.

ries.* Compare this with the algebraic sum of the heats of reaction in the cell and if these quantities are equal the conversion is complete.

This condition is very nearly exactly realized by the Daniell cell, which it will be remembered was cited as typical of the " reversible " class. In this cell zinc dissolves and forms a solution of $ZnSO_4$. The heat of formation of this solution from $Zn + O + SO_3 + Aq$ = 106 090 cal. Copper comes out of a solution of $CuSO_4$. The heat of formation of a solution of $CuSO_4$ from $Cu + O + SO_3 + Aq$ = 55 960 cal. As this latter reaction occurs in the opposite way, we must subtract the heat of formation of $CuSO_4$, Aq. from that of $ZnSO_4$, Aq. to find the available heat of the cell in action. We thus have 50 130 cal., which may be converted to electrical energy. The valence is 2, so $n = 2$. Substituting these values in our equation, we have

$$\pi = \frac{4.183 \times 50\,130}{96\,500 \times 2} = 1.086 \text{ volts.}$$

This is almost exactly the e.m.f. of the Daniell cell when directly measured.

The Temperature Coefficient. We may secure an exceedingly interesting and significant formula by following through a cyclical process such as was first considered in Chapter XXII. Suppose we have a reversible cell with an e.m.f. of π volts immersed in a large reservoir which we shall call number one, at the temperature T. Let F represent Faraday's constant, and n represent the valence of the metal electrode. Now send a quantity of electricity nF through the cell. The total electrical energy is then $nF\pi$. If it is all converted quantitatively to chemical energy, there is no heat effect. But suppose the electrical energy to be a little in excess of the chemical as measured by the heats of reaction. This excess will become heat, and let us say that in this way a quantity of heat, W, is given to the reservoir.

Now transfer the cell to a second large reservoir, number two, which is at the temperature $T + dT$. If K be the heat capacity of the cell, it will take up a quantity of heat KdT, and we shall assume that its electromotive force has increased by an amount $d\pi$ and has become $\pi + d\pi$.

* CE = total electrical energy, and the heating effect in a resistance wire is proportional to it. $C = \frac{E}{R}$. Therefore $E = CR$. Substitute this value for E and we have C^2R, or, the heating effect varies directly with the resistance, and directly with the square of the current (amperes).

Now cause the cell to give out the quantity nF coulombs. It does this with the intensity $\pi + d\pi$, and so the total energy obtained is equal to $nF(\pi + d\pi)$, and at the end of the process the cell is in its original condition chemically. During this reverse process the cell has taken up from reservoir number two a quantity of heat, W, the same which it gave to reservoir number one. Now put it back in reservoir number one, where it will give up the quantity of heat KdT and will be exactly where it started, having completed a cycle.

The whole process amounts to the transference of a quantity of heat, W, from the temperature $T + dT$ to the temperature T. KdT is negligibly small in comparison with W.

We learned in Chapter XXII that in such cyclical processes the maximum amount of heat which we can get converted into work (dQ) is given by the expression $dQ = Q\frac{dT}{T}$, where Q is the total heat transferred and dT is the difference in temperature between the two reservoirs. The electrical work which we gained in our process is the difference between the two total electrical energies, or

$$nF(\pi + d\pi) - nF\pi.$$

This equals $nFd\pi$. The total heat transferred was W. Substituting these values, we have $nFd\pi = W\frac{dT}{T}$. Transposing, we have

$$\frac{d\pi}{dT} = \frac{W}{nFT}.$$

The amount of heat, W, which reservoir number two had to supply is equal to the electrical energy given by the cell less the heat of the reaction (H). Then $W = nF\pi - H$. Substituting this value, we have $\frac{d\pi}{dT} = \frac{nF\pi - H}{nFT}$. This is the same as $\pi = \frac{H}{nF} + T\frac{d\pi}{dT}$, a formula known as Helmholtz's equation. $\frac{d\pi}{dT}$, expressing the change in e.m.f. with change in temperature, is the temperature coefficient of the cell.

If the temperature coefficient of a cell is zero, if its e.m.f. is not altered by altering its temperature, the second term of Helmholtz's equation becomes equal to zero, and we have $\pi = \frac{H}{nF}$ (multiplied by the factor 4.183 to convert calories to joules, of course). This is the formula we used in calculating the e.m.f. of a Daniell cell, and the calculated results agreed well with the results of experiments. This indicates that the temperature coefficient of the Daniell cell is very

nearly zero, and this also has been found by experiment to be the fact.

If the e.m.f. of a cell decreases as the temperature is raised, $\frac{d\pi}{dT}$ is a minus quantity. $\frac{d\pi}{dT} = \frac{W}{nFT}$ and so W must also be a minus quantity. $W = nF\pi - H$, and therefore H must be greater than $nF\pi$. Translated into words, this means the heat of the reaction must be more than equivalent to the electrical energy; that is, the cell must grow warmer when it works.

Suppose the e.m.f. of the cell increases with the temperature. Then $\frac{d\pi}{dT}$ is positive, W must be positive, $nF\pi$ must be greater than H, and we must get more electrical energy than is equivalent to the heat of the reaction. This cell must cool off when it works.

Such a cell thus delivers useful work at the expense of its own internal energy and, cooling off, must take up heat from the surroundings. This is not to be considered as an exception to the second law of thermodynamics because the process is not reversible. To bring the cell back to its original condition we must give it electrical energy enough to reverse the chemical reaction, and we cannot do this without simultaneously heating it, and causing it to return to the surroundings all the heat it took up.

Ostwald made an interesting deduction from the foregoing considerations. If the temperature coefficient of a cell is a minus quantity, then by raising the temperature sufficiently, the e.m.f of the cell may be made to pass through zero, after which the poles will be reversed. Furthermore, the higher the temperature, the greater the value of the term $\frac{d\pi}{dT}$, until it may grow very great in comparison with the purely chemical term $\frac{H}{nF}$. In other words, the chemical process may become, as it were, a side issue. Practically all the heat furnished such a cell at constant temperature from outside would be converted with small loss to electrical energy. We know no such cell. It may be considered as the element of the future, the long-sought device to convert heat directly into electrical energy on a large scale.*

* This will infallibly call to mind "thermoelements." The e.m.f. obtained upon heating the junction of two metals is so small we have not yet succeeded in developing it into a practical source of current.

It will be well to remind the reader that these formulæ we have been discussing apply only to reversible cells. But, after all, every cell is reversible to some extent at least, as is proved by the fact that alternating currents show no deviation from Ohm's law in passing through them.

Storage Cells. Storage cells are indispensable in the laboratory, and evidently destined to be more and more widely used at telephone and telegraph stations, at lighting stations to equalize loads, and on automobiles. It therefore seems desirable to devote a few pages to their consideration in some detail. Any reversible element is a storage cell, or accumulator, as it is often called; for it stores up or accumulates the electrical energy sent into it in the form of chemical energy, and will give it back when the process is reversed. For example, the Daniell cell is a storage battery, but for various reasons it is not used in that capacity.

Counting all the different modifications of electrolyte and electrodes, it is safe to say there are several hundred different combinations which have been tried and have been found to be moderately satisfactory.*

The Lead-Sulphuric Acid Cell. Curiously enough, only two of these possibilities have been found practically useful, and of these two the lead-sulphuric acid cell is the better known, and the only one thoroughly tried out under all conditions of actual service.

Gaston Planté, in 1859, immersed two lead electrodes in dilute sulphuric acid and sent a current through. At first hydrogen goes off as a gas at the cathode, while a portion of the anode is oxidized to PbO_2. If now the current is sent through in the opposite direction, the hydrogen, instead of being evolved as a gas, reduces the PbO_2 to a spongy form of lead, and PbO_2 is produced at the other electrode. The more often this alternation is carried out the greater the quantity of spongy lead and of PbO_2 produced at the end of a "charge." This is known as Planté's method of "forming" the electrodes. It must be done slowly and requires about three months to produce a good, useful cell. At the end, however, we have the most efficient storage cell of which we know, consisting of one electrode of spongy lead and one of PbO_2, both in dilute H_2SO_4.

Many ingenious plans have been tried for diminishing the time re-

* For a thorough survey of the subject see "Die Akkumulatoren für Elektricitat," by E. Hoppe, third edition, 425 pp. (1898); and "Die Theorie des Bleiaccumulators," by F. Dolezalek, 122 pp. (1901).

quired for "forming" the plates. The general principle is always the same. Grooves are cut, or holes are bored, in lead plates, and these grooves or holes are mechanically filled with some compound of lead which, upon electrolysis in sulphuric acid, will give spongy lead at one electrode and lead peroxide at the other.

The names under which cells are marketed are sometimes misleading, perhaps intentionally so, to produce the impression on the purchaser that some fundamentally new principle has been discovered. For instance, the so-called "chloride" cell contains no chlorine. Lead chloride is used in filling up the leaden framework in the first place, but it is converted to spongy lead and lead peroxide before it is ready for the market. We cannot spend time upon details of manufacture, and it will be sufficient to repeat that differences of name refer without exception to these details, and every lead storage cell is like every other, in that it consists of electrodes of spongy lead and lead peroxide immersed in dilute sulphuric acid. The cell may consist of a number of plates, if it is desired to increase its capacity. On the outside is a gray, spongy lead plate, next a brown peroxide plate, next a gray, spongy lead plate, and so on. But there is always one more spongy lead plate than peroxide plates. All the peroxide plates are connected together, and, since the plus current comes out of this wire, when the cell is delivering current, these are called the positive plates. All the spongy lead plates are connected together, and this connection being the negative terminal when the cell is discharging, these are called the negative plates.

The filling material is called the active mass, and even in the best of cells, and with the best of care, portions of it become loosened and fall. This would short-circuit the cell and quickly ruin it if the plates reached to the bottom. On this account the plates are suspended from the top, in the jar containing the acid, and are kept separate by rods or rings of hard rubber.

This gradual loss of active mass is not so serious as one might imagine, because the repeated charging and discharging the cell receives in use amount to the Planté method of "forming." More and more of the lead framework thus becomes "active mass" replacing the loss. Indeed, it is not unusual to find a cell has improved after use.

When the cell delivers a current, the spongy lead and the lead peroxide are both converted to lead sulphate. We may write: $Pb + 2\,H_2SO_4 + PbO_2 = 2\,PbSO_4 + 2\,H_2O$, and we may write the

reverse reaction for the occurrences when charging. The sulphuric acid is thus used up during the discharge and recovered on the charge. One way to estimate how far a cell is discharged is by determining the specific gravity of the electrolyte. This is evidently greatest when the cell is fully charged and least when fully discharged.

The e.m.f. of the cell is a function of the concentration of the acid, and the following table shows this relation:

Specific gravity of acid.	Per cent H_2SO_4	e.m.f.
1.496	58.37	2.27
1.415	50.73	2.18
1.279	35.82	2.05
1.140	19.07	1.93
1.028	3.91	1.83

The best results are obtained with plenty of acid of sp. gr. 1.180 to 1.200 in the fully charged cell, but greater concentrations are sometimes recommended.

Immediately after charging, the e.m.f. is high, perhaps 2.4 volts, but it sinks rapidly to nearly 2 volts. Here it remains very constant for a long while, which is one of the great advantages of the cell. Then it falls slowly to 1.8 or 1.7 volts, after which the drop is rather rapid to zero.

The explanation of this behavior is as follows: The cell is charged until gases are given off. Hydrogen and oxygen are then absorbed and cling to the electrodes, and it is these which cause this very high potential. As soon as they are used up, we have the reaction of the cell proper, with its corresponding electromotive force of 2 volts, until the active material is gone.

In order that the electromotive force may be constant, we must have plenty of sulphuric acid, for this is used in the discharge, and if there is only just enough for the purpose, the concentration of the acid falls too rapidly, and this is accompanied by a fall of potential, as indicated in the table. The least allowable quantity is 25 $cm.^3$ of sulphuric acid of a specific gravity of 1.15 per ampere-hour.

Amount of Material Used in the Storage Cell. The amount of material requisite in a storage cell is readily calculated from the reaction with the aid of Faraday's constant. For 1 ampere-hour we must have 3.87 grams of lead sponge, 4.47 grams of lead peroxide, 3.67 grams of sulphuric acid, corresponding to about 18 grams of sul-

phuric acid of specific gravity 1.15. As a result of the reactions for 1 ampere-hour, we obtained 11.31 grams of lead sulphate. Some sulphuric acid must be left in order that the liquid shall conduct.

The Efficiency of Storage Batteries. The amount of energy which we can recover again from a storage battery may be measured in two ways, either as ampere-hours, or as volt-ampere-hours. If we use ampere-hours, we are dealing with the capacity factor, the quantity, alone. If we wish to know the total energy, we must use volt-ampere-hours (watt-hours), and this is the only true test of the efficiency of a storage battery. By the ampere-hour test the cells make a good showing. In the discharge, we get back between 90 and 96 out of every hundred ampere-hours put in. In other words, the "efficiency" is between 90 and 96 per cent. But if we use the true test, the volt-ampere-hours, the results are not so good. The "efficiency" is between 76 and 88 per cent. The cause of the difference is perfectly obvious. The voltage of the charging current is, and necessarily must be, a little higher than the voltage of the cell. The following table gives a typical set of measurements upon a storage cell, charging and discharging.

	Ampere-hours.	Watt-hours.
Charging time, 9.2 hours. Average amperes, 2.4. Average voltage, 2.16.	9.2×2.4 =22.08	9.2×2.4×2.16 =47.68
Discharging time, 4.6 hours. Average amperes, 4.5. Average voltage, 1.98.	4.6×4.5 =20.70 or 93.7 per cent	4.6×4.5×1.98 =40.99 or 85.9 per cent

The efficiency is also in a great degree dependent on the rate at which the current is taken off. Suppose we take off a large current rapidly; the reaction must keep pace. But the active mass and the acid in immediate contact may get used up and the reaction cannot proceed until more acid has, by diffusion, come in contact with more active mass. Diffusion is rather slow.

To give time for diffusion the following rules are useful: The charging current should be so regulated that it will give the cell its whole charge in not less than 5 hours. A good average rate is one that will charge the cell in 10 hours. The discharging current should empty the cell to 1.8 volts in not less than 4 hours. The best rate of discharge is one that requires 8 hours. Experience has

demonstrated that it is possible to discharge storage batteries faster than we can charge them. There is no theoretical explanation for this.

Cells are advertised and sold by guaranteed ampere-hour capacities. Suppose a cell has a capacity of 20 ampere-hours. A 2.5-ampere current will give it its full charge in 8 hours and is a suitable charging current. Five amperes is the maximum to take from such a cell. Contrary to the general idea, it does not damage a cell to overtax it for a brief time. It is a waste of energy, for then we get back only a small per cent of what we put in; but this overtaxing must last only for a short time.

The lead sulphate which forms when a cell is discharged is not the ordinary white crystalline variety. It is different, and we do not know very well wherein the difference lies, but we do know the variety formed is readily reduced to lead at one electrode and oxidized to lead peroxide at the other, while the crystalline substance is not. If the lead sulphate becomes crystalline, the cell is damaged; it is said to be "sulphated." If this "sulphating" has not gone too far, a long, slow charge will rectify the trouble.

Three Ways to Damage a Storage Cell. If a cell is exhausted until it shows an e.m.f. of 1.7 volts or less, it appears that crystalline $PbSO_4$ forms readily in the interior of the plates, between the active mass and the framework. As crystalline $PbSO_4$ is an exceedingly poor conductor, the contact is destroyed just there, and it is next to impossible to oxidize it or reduce it again. Its formation is accompanied by an increase of volume, and this pries loose the active mass, thus reducing the capacity of the cell almost indefinitely.

If impure sulphuric acid is used, foreign metals will deposit on the plates and set up local electrolytic actions which do serious damage. It is very easy to purify the acid. Dilute it; run in H_2S; filter off the precipitate; drive off excess H_2S by boiling. Small amounts of H_2S left in the acid do no harm, and, moreover, are soon destroyed in the course of charging and discharging. We can detect the presence of impurities in the acid from the appearance of the minus plates. If impurities are present they become dark gray or dirty gray instead of silver gray, as they should be. If the damage has gone far there is no remedy, and new negative plates must be secured.

A third quick way to ruin a storage cell is to short-circuit it or otherwise draw off too large a current for a time. (For instance, connect it wrong end to for charging.) The unduly rapid reactions proceed faster in some places than others, and, being accompanied

by volume changes, loosen the active mass and even bend the heavy framework. An exceedingly brief short circuit will do no perceptible harm. Remembering how the deterioration is produced, one can easily realize it is directly proportional to the duration of the short circuit.

Cells at rest gradually discharge. There are two reasons for this. First, the insulation is never perfect. The edge of the glass is wet with dilute sulphuric acid, this conducts, and a small current is thus always passing. Secondly, the oxygen of the air dissolves, and sulphuric acid containing oxygen converts the minus plate to lead sulphate without a current It usually takes months, though, to produce much effect in this way. The lead sulphate normally present in the cell is probably an allotropic modification of the more familiar variety. It may change over in the course of time. For all these reasons, cells should not be left standing unless fully charged, and when not in use they should be discharged and recharged every two or three months.

Joining Cells for Use. Having a number of cells, we may join them in series and obtain a voltage the sum of all the cells. But then we must keep the amperage down to the maximum of one cell. We may join them in parallel, obtaining the voltage of one cell, but then we may take off an amperage equal to the sum of the capacities.

Horse Power of Cells. One horse power equals 746 watts. Assume that we have a battery of 5 cells, each of 80 ampere-hours' capacity joined in series. The e.m.f. is then 10 volts, and if we discharge at a 10-ampere rate we are drawing off 100 watts. This gives us $\frac{100}{746}$ horse power, or about $\frac{1}{7}$ of a horse power for 8 hours.

It is very unfortunate that for a given capacity these cells weigh so much. While there is some difference between makes, it is a fair average to say that an 80 ampere-hour cell of the laboratory type weighs about 12 kilos. Since the e.m.f. is 2, this cell will give 160 watt-hours, or 13.3+ watt-hours per kilogram. In the portable type, as used in electric automobiles, hard rubber is used in place of glass, and the weight is somewhat reduced, but not much, for we always have to have such a large excess of acid and of lead, which take no part in the actual reactions.

The Temperature Coefficient of Storage Cells. For a time it was supposed that the temperature coefficient of a storage cell was equal to zero. This would indicate that all the chemical energy was

converted without loss to electrical energy. But recent careful investigations have shown that there is a temperature coefficient, and that it is, with most acid concentrations, plus.* In the formula $\pi = \frac{H}{nF} + T\frac{d\pi}{dT}$, $\frac{d\pi}{dT}$ then has a plus value. The electrical energy must slightly exceed the chemical, and the cell must cool a little as it discharges.

The suggestion has been made that we might construct the following machine: Have cell A warm and cell B cold. A then has a higher e.m.f. than B, and if the two are connected A will charge B and will give it slightly more charge than it had itself, at the cost of the heat of the surroundings. Now change their positions and permit B to charge A and make an additional gain. Such a machine would convert heat directly into electrical energy, a much-desired arrangement. The difficulties are great and the device not practical.†

The Nickel-Iron-Alkali Cell. The only really different storage cell which has been perfected until practical is that generally known as the Edison cell. The negative plate is a nickel-plated grid with flat rectangular pockets containing finely divided iron. The positive plate is another nickel-plated framework holding together many perforated tubes, about the diameter of a lead pencil and half its length. These tubes are packed with peroxide of nickel, NiO_2, and also contain electrolytically prepared flakes of pure nickel to increase the conductance. The electrolyte is a 20 per cent solution of potassium hydroxide.

Exactly what the chemical changes are in this cell cannot be considered as definitely settled. The iron is oxidized, probably in part to one stage, in part to another, with the formation of corresponding hydroxides. The nickel peroxide is reduced, and this also probably occurs with the formation of several different hydroxides. Water actually enters into the reaction, being used up as the cell discharges, and again formed when the cell is charged. In one experiment one liter of solution became 950 cm.^{3} after the discharge.

The following table contains data upon this cell:‡

* F. Dolezalek, *Zeitschr. f. Elektrochem.*, **6**, 517–519 (1900). If the acid is less than 0.0005 normal the coefficient is minus.

† The reader must realize this could not by any chance be a "perpetual motion" machine. Heat is transferred from a higher to a lower temperature, and wherever this happens we can get some work done, the maximum being the "economic coefficient" defined in Chapter XXII.

‡ *Electrical World*, **55**, 175–177 (1910).

	Type A-4.	Type A-6.
Rated output in ampere-hours	150	225
Average discharge voltage per cell	1.2	1.2
Normal rates of charge and discharge, amperes	30	45
Efficiency, 60 to 65 per cent.		
Watt-hours per kilogram of cell	30.8	35.2

According to these figures a battery of Edison cells is much lighter than a battery of lead cells for a given horse power, but it is more wasteful of charging current. The claim is made that it is more durable, and that short-circuiting does not hurt it. On the other hand, as chemists well know, the handling of alkalies is fraught with more possibilities of disagreeable incidents than the handling of acids. Potassium hydroxide takes up carbon dioxide from the air to form carbonate, and must be renewed occasionally, or the cell must be closed almost air-tight. The e.m.f. of the lead cell is very constant, that of the Edison cell is not, and is lower, therefore the latter will hardly replace the former in laboratories or for stationary batteries.

CHAPTER XXX

ACTINOCHEMISTRY

RADIANT energy has been subdivided for purposes of study into heat, electricity, and light. All three travel through space, containing no other form of energy known to us, at the same rate (300,000 kilometers a second), and the only difference we have succeeded in establishing between them is one of wave length. These wave lengths were given in the form of a chart in Chapter VIII, and from this it is evident enough that our subdivision is arbitrary.

We know very little regarding radiant energy as such, and cannot even divide it into an intensity and a capacity factor. As was brought out in earlier chapters, we incline to attribute to it an " atomistic " or granular structure, and think of it as electrons in motion. We may paraphrase the quotation from Kekulé in Chapter V and say, " Whether radiant energy be electrons or not, this much is certain, that, granting it to be electrons, it would appear as it now does."

Depending upon the wave length, radiant energy produces different effects. It is these effects we measure and which really are at the basis of our classification. Having treated of thermochemistry and of electrochemistry, it remains to consider the transformations of chemical energy on the one hand, and that portion of radiant energy called light, on the other. But the rays which are most effective chemically, the so-called actinic rays, are of such short wave lengths they do not affect the retina of the eye, and so we talk of invisible light,—a clever paradox, useful to stimulate the curiosity of beginners. Once more we see how the old-time boundaries are broken down and how impossible it is to definitely delimit any branch of science.

Much has been said in previous chapters concerning light, and need not be repeated. In this chapter we shall consider a few important topics not yet discussed. The subject is usually called photochemistry, but that term is also used to denote the art of photography, which comprises only highly specialized applications of a few of the important facts, and so the title " actinochemistry " is preferable.

First, let us dispose of a dream which has been entertained by

some. We can bring the rays of the sun to a focus by means of a "burning glass" and set fire to objects. It might appear possible, by some system of lenses, to bring radiant energy to a focus in such a way that this focus should have a higher temperature than the source. This would be raising heat to a higher temperature without expending energy upon it, and could be made into a "perpetual motion" machine. The second law of thermodynamics tells us this is impossible.

Radiant energy impinging on an object is in part reflected, in part absorbed and converted to other forms, and part may pass through unaltered. It exerts a pressure, as has at last been definitely proved. This pressure is a small quantity; the pressure of the radiations from the sun on the earth is equivalent to the pressure of a column of water two-millionths of a millimeter high. This is an entirely negligible quantity in all our measurements. But on an exceedingly small, light object—for instance, molecules of a highly rarefied gas—it may not be negligible.*

The processes upon earth are all accompanied by a loss of free energy, and our planet would quickly become uninhabitable were it not for the new supply of free energy constantly being received from the sun. Our earth intercepts but a small fraction of the sun's whole radiation, and but a small fraction of this ever becomes available for us. Most of it goes to maintain the average temperature of the earth's crust, counterbalancing the earth's radiation into space.

It has been estimated by Le Chatelier† that the radiant energy from the sun is equivalent to 2 100 000 calories per square meter per year. The quantity of carbon in the various compounds resulting from luxuriant vegetation is about 100 grams per square meter per year, and burning this evolves about 800 calories; that is, vegetation stores up, in a form useful to us, about $\frac{1}{100}$ of 1 per cent of all the radiant energy it receives. He further estimates that if all the radiant energy could be converted without loss to mechanical energy, it would equal about one-third of a horse power per square meter. In spite of many efforts, no practical machine has as yet been invented for the conversion of solar energy into mechanical. Such extensive areas must be covered, the first cost of the apparatus is too great. The devices to convert the sun's energy into electrical energy have an efficiency practically equal to zero.

* See Arrhenius, "Das Werden der Welten."

† Le Chatelier, "Leçons sur le Carbone," p. 112.

Le Chatelier's conclusion is that we can hardly hope to obtain an efficiency greater than one per cent of the radiant energy, and even so good a machine as that would require an exposure of 300 square meters for one horse power. Thus, to supply a factory requiring 10 000 horse power, the generator, or collector, would have to cover 3 square kilometers. It is well to bear in mind these figures, in view of current newspaper articles and second-class mail which are calculated to make those unfamiliar with the actual facts believe the problem solved. We may soon have occasion to add another to the Keely motor, gold-from-sea-water, cold-storage-with-liquid-air series of fiascos.

If one form of energy can be considered as more important than another, radiant energy must certainly head the list. The subject in hand is, then, perhaps the most important we have taken up. And yet we know less about the transformations between radiant and chemical energy, how to produce them and how to increase them to maximum efficiency, than about the transformations between any other pair of forms. We cannot even subdivide radiant energy satisfactorily into intensity and capacity factors. We have few great generalizations but many isolated facts. These facts are far from uninteresting; indeed, the whole subject is really all the more fascinating because of its incompleteness and its consequent immense possibilities. Let us consider some of these facts in detail.

Photochemical Absorption. When radiant energy is absorbed by a substance, part is converted to heat and part may produce chemical changes. When this last conversion occurs, we have an instance of "photochemical absorption." The portion so converted is always small, and its quantity varies greatly with the nature of the substance and with the wave length of the radiant energy.

Photochemical absorption is a more frequent phenomenon than is commonly realized. For instance, sunburn is an interesting, if sometimes painful, example. The light determines the formation of a pigment in the skin, which then grows brown and more opaque to rays which might injure deeper tissues. Light complexions are native to northern countries where the sunlight is less intense. Many find certain kinds of light trying to the eyes. The physiological effect of light is an important subject, still in its infancy. When colors fade, bleaching in the sunlight, we have instances of photochemical absorption. Photochemical absorption precedes the formation of chlorophyll, the green coloring matter of vegetation; and

plant growth in the dark produces substances different from those formed by plant growth in the light.

Some Reactions Influenced by Light. The reaction $H_2 + Cl_2 = 2HCl$ is much hastened by light. White phosphorus exposed to sunlight changes to the red allotropic modification, and this occurs whether the phosphorus is under water, alcohol, ether, oils, in an atmosphere of hydrogen, or in a vacuum. Red mercuric sulphide, HgS (cinnabar), turns black in sunlight. This change is probably a chemical decomposition; the presence of a trace of moisture is necessary; it does not occur under acids; it occurs more rapidly under alkalies than under water. A water solution of hydrogen peroxide is decomposed by light; chlorine, dissolved in water, when exposed to light forms hydrochloric acid with the evolution of oxygen; concentrated nitric acid is decomposed by light; phosphine in the sunlight decomposes, and free phosphorus is deposited; chromates in contact with organic substances are reduced, and the reduction is more rapid if the substances are dry than if they are wet. An insoluble compound is formed by this reaction when potassium dichromate is mixed with gelatine. White silver chloride turns dark when exposed to light, and this change is effected most rapidly by violet light. The changes produced in the halogen salts of silver (first noticed by Scheele in 1777) form the basis of our photographic processes.

Saturated hydrocarbons are not altered by light, but every unsaturated hydrocarbon without exception is altered. For instance, acetylene is changed to benzene, and this in turn to a solid substance.

It is evident from the above assortment of facts that radiant energy can act in many ways; it can cause combination, and decomposition, oxidation and reduction, and polymerization. In general it hastens reactions, but it can also retard reactions. It is, then, often a positive, but sometimes a negative, catalytic agent. For instance, the oxidation of pyrogallol by oxygen is hastened by red light, but retarded by violet light.* It has been found to be a fairly general rule that red light oxidizes metallic compounds, while violet light reduces them. No case has yet been found where violet light certainly oxidizes a metallic compound.

Almost always changes brought about by light are changes which evolve heat; *i.e.*, changes to a more stable form; and a majority of the changes produced by light may be reversed by heating the product.

* Trautz, *Physikal. Zeitschr.*, 7, 899 (1906).

In all cases, the quantity of the photochemical action depends on the wave length of the light, and in most cases the shorter the wave length the greater the photochemical effect.*

Formation of Hydrogen Chloride. The most thoroughly investigated photochemical reaction is the combination of a mixture of hydrogen and chlorine to form hydrogen chloride. In the dark and cold, the combination proceeds at an imperceptible rate; in bright sunlight, or the light of burning magnesium, with explosive velocity,—an experiment always shown in first courses on chemistry. This effect was first observed by Berthollet, then studied systematically by Draper, and then more thoroughly by Bunsen and Roscoe.†

Actinometer. A mixture of hydrogen and chlorine, in equimolecular quantities, was exposed to light sufficient to cause the reaction to proceed at a convenient rate. As fast as formed, the hydrogen chloride was dissolved in water, and the diminution in volume of the gas was a measure of the effect of the light. Such an instrument, measuring the light effect, is called an actinometer.

Draper threw the light from an evenly illuminated white screen on his actinometer by means of a lens. He partly covered his lens, and found the quantity of the reaction was directly proportional to the quantity of light, thus demonstrating a fundamental law.

Photochemical Induction. Bunsen and Roscoe found that under constant illumination the velocity of formation of the hydrogen chloride gradually increased to a maximum and then became constant. This phenomenon is called photochemical induction; and the time, from the start till the maximum constant velocity is reached, is called the induction period. In one of their experiments, with an oil lamp, the time was nine minutes. This phenomenon is probably due to the presence of small traces of oxygen which act as a negative catalyzer upon the chlorine.‡ After the reaction has proceeded for a while, this oxygen and its retarding influences are removed. In-

* For lists of photochemical reactions see Eder, "Handbuch der Photochemie," 1906. Fehling's "Handwörterbuch der Chemie," article on Light. M. Roloff, "Uber Lightwirkungen," *Zeitschr. Phys. Chem.*, **26**, 337–361 (1898). G. Ciamician, "Actions Chimique de la Lumière," *Bull. Soc. Chim. de France* (4), **3**. Lecture delivered June 6, 1908, dealing with action of light on organic substances. Bound in at end of volume; 28 pp.; not paged consecutively with the rest.

† R. Bunsen and H. E. Roscoe, "Photochem. Untersuchungen," *Poggendorf's Annalen.*, **96**, 373 (1855); **100**, 43 (1857); **101**, 275 (1857); **108**, 193 (1859). Reprinted in Ostwald's "Klassiker der exakten Wissenschaften," No. 34 and No. 38.

‡ R. Luther and E. Goldberg, *Zeitschr. f. phys. Chem.*, **56**, 43 (1906).

duction periods have been observed in numerous other photochemical reactions.*

The Fraction of Radiant Energy Converted to Chemical Energy. Bunsen and Roscoe sent light from a constant source through a layer of pure chlorine, and determined how much of the energy was absorbed. They then substituted a mixture of equal volumes of hydrogen and chlorine twice as thick, thus having the same thickness of chlorine. Hydrogen absorbs practically none of the radiant energy, but in this second experiment they found considerably more absorbed. This excess was then a measure of the quantity of radiant energy which was used in causing the formation of hydrochloric acid. They concluded that, of the radiant energy absorbed by a mixture of hydrogen and chlorine, two-thirds went to heating the gases and one-third to putting the gases in condition to react with each other.

Photochemical Extinction. Light will act on a substance only if it is absorbed by the substance. Bunsen and Roscoe found that if light is passed through a layer on which it acts photochemically, and then enters a second similar layer, its action on the latter is less than if it had not traversed the first. They call this photochemical extinction.

Silver Chloride Actinometer. Any instrument or substance which measures the chemical action of light is called an actinometer, and the hydrogen-chlorine mixture we have discussed is typical. It does not give us results in absolute measure, and actinometers to do this have not, as yet, been contrived. They give only results which are approximately proportional to each other.

A rather crude device, sometimes used in photography, is the silver chloride actinometer. Paper is coated with silver chloride; a portion of it is exposed to the light, and the time required by the chloride to darken to a definite shade is noted. Twice as long a time indicates half as much light, etc.

Mercuric Oxalate Actinometer. The following reaction occurs in light: $2\,HgCl_2 + C_2O_4(NH_4)_2 = 2\,HgCl + 2\,CO_2 + 2\,NH_4Cl$. The volume of carbon dioxide may be measured, or the precipitated mercurous chloride may be weighed. The results are proportional to the light.

* C. H. Burgess and D. L. Chapman, *Jour. Chem. Soc.*, London, **89**, 1399–1434 (1906), found no evidence of a photochemical induction period with a moist mixture of chlorine and hydrogen free from impurities. They found that small traces of NH_3 or of SO_2 inhibited the reaction.

Electrochemical Actinometer. The following arrangement was first used by Becquerel in 1839: Two silver electrodes are coated with chloride or iodide of silver and are immersed in dilute sulphuric acid. One electrode is in the dark, the other is exposed to the light to be measured. An electrical current passes in the solution from the dark to the light electrode, and, measured by a galvanometer, is a measure of the light. A simpler form consists of two copper electrodes slightly oxidized in a bunsen burner and immersed in a one per cent solution of common salt.*

Selenium. The conductivity of a wire of selenium is perhaps ten times as good in bright sunlight as in the dark. This might be used as an actinometer, but the property varies much between different samples of selenium. We know very little as to the cause of this exceptional property. Perhaps it is due to the presence of an impurity. It has been utilized in isolated cases for automatic alarms.

Sending Photographs and Writing by Telegraph. The alkali metals, sodium, potassium, and lithium, when exposed to light, send out ions which cause a gas above them to conduct. When the light departs the conducting ions disappear at once. Two metallic plates may be arranged above a surface of sodium in such a way that they are in an electric circuit. If an image of writing or the like is projected and caused to pass over the opening between the plates, the light and darkness are translated into fluctuations of the electrical current. These fluctuations may be caused to actuate a pen or pencil on a paper moving at the receiving station synchronously with the image at the sending station.

Photography. Photography has sometimes been held to deserve no place in a strictly scientific book, because it is only a number of variations of few scientific principles highly developed in their applications. The art has outrun the science, but this is not a logical reason for excluding it; on the contrary, special attention should be drawn to it, that the science may catch up. It contains many extremely interesting unsolved scientific problems. It is a most useful art, particularly useful in science to record and disseminate results, almost as useful as the art of printing itself. It is in one sense typically a physical-chemical subject. The camera, lens, and formation of the image are applications of physics, while the registration and fixation of this image are applications of chemistry. The product of

* H. Rigollot, *Jour. de Physique* (3), 6, 520–525 (1897), and "Recherches expérimentales sur quelques Actinomètres electro-chimiques," 138 pp., Lyons (1897).

the combination is an illustration of the practical value of the results obtainable by coöperation of the sciences.*

Historical. Leonardo da Vinci described a pinhole camera-obscura, but did not claim the device as his invention, nor even as anything particularly new. In 1810, Seebeck, professor of physics at Jena, published observations upon colors produced in silver chloride by the spectrum.

The first process for the production of photographs, as we understand the word, we owe to Nicéphore Niepce and Daguerre, who made their discovery in 1829, devoted ten years to efforts at perfecting the process, and announced it in 1839. The process of telegraphy was invented at about the same time, by Gauss and Weber, in Göttingen, in 1833, and several writers have commented upon the much greater rapidity with which telegraphy developed, both scientifically and practically, than photography.

Daguerre's Process. Daguerre's process was as follows: A highly polished silver plate was given a thin layer of silver iodide and was then exposed in a camera. The development consisted in holding the exposed plate over the vapor of mercury, when the mercury deposited in largest amount where the light had acted most, and thus the image was produced. By this process one exposure gives but one picture, and copies cannot be made. Such a picture is not permanent. Though it may be made to last for some years if properly cared for, yet eventually it disappears. The principles at the base of Daguerre's process are probably capable of useful development, but such development has not as yet been forthcoming, and the process is now abandoned.

Wet Plate Process. The next advance consisted in the invention of the collodion, or "wet plate," process. Glass is covered with a thin coat of collodion containing a halogen salt. Just before the exposure is to be made this plate is treated with a solution of silver nitrate, which forms the halogen silver salt within the collodion.

* The standard authority upon this subject is J. M. Eder's "Ausführliches Handbuch der Photographie," an extensive work. R. C. Bayley's "The Complete Photographer," 410 pp. (1906), is a particularly readable text. Other books which may be recommended are as follows: R. Luther, "Die Chemischen Vorgänge in der Photographie," 96 pp. (1899). H. W. Vogel, "Photochemie und Beschriebung der photographischen Chemikalien," 376 pp. (1906). Lüppo-Cramer, "Kolloidchemie und Photographie," 154 pp. (1908). L. Derr, "Photography for Students of Physics and Chemistry," 243 pp. (1906). R. Meldola, "The Chemistry of Photography," 382 pp. (1901).

While still wet the plate is exposed in the camera, taken to the dark room, and treated with another solution of silver nitrate to which has been added a reducing agent. Where light has acted, silver nitrate of the developer is reduced and metallic silver is deposited. In this way the image is built up out of silver obtained from the developer. The unchanged halogen salt is dissolved out with a solution of sodium thiosulphate, and thus a permanent negative is obtained.

These " wet " plates require much longer exposures in the camera than the " dry " plates, and are far less convenient, because a dark room must be at hand when an exposure is made. Therefore the process is not generally used. It finds an application, however, in certain technical processes of reproduction, because the grain of the silver deposit is finer than that obtainable by the " dry " plate process.

The Dry Plate Process. The dry plates or films now universally used consist of a colloidal solution of a halogen salt of silver in gelatine, spread on a glass plate or a celluloid film.

A solution of gelatine containing silver nitrate is mixed with a solution of gelatine containing potassium bromide. Exceedingly fine particles of silver bromide are thus formed, and remain in suspension as a colloidal solution. This is allowed to solidify, and is broken up into small pieces and washed to remove the excess of silver nitrate. It is then remelted, and is ready to coat the plates. But such plates would not be particularly sensitive.

Ripening. The emulsion, as it is called, is allowed to " ripen," a process which was described in Chapter XIX. The particles of silver bromide increase in size, slowly at low temperatures, rapidly at high temperatures. The larger the particles the more sensitive they appear to be to light. At the same time, the larger the particles the coarser-grained the resulting negative, and so the ripening process must not be pushed too far. Microscopic examination with relatively low powers will show that negatives made upon extremely rapid plates are coarser in grain than those made on slow plates. If the ripening is continued too long the plates are too sensitive, and the change produced by light takes place slowly even in the dark; and such plates when developed are " fogged," *i.e.*, coated with an even deposit of metallic silver.

Light appears to produce an effect very similar to this ripening process, and a plate itself not sensitive can be made much more sensitive by an exceedingly brief exposure to light. There is, as it were, a

threshold which must be crossed before the action of light is of such a character that we can make it permanent by our chemical processes.

Action of Light. When a plate thus prepared is exposed in the camera, the silver bromide is, in a measure, reduced. That free bromine is given off has been demonstrated experimentally. It is generally conceded that the other product is a compound with a formula Ag_2Br, but this compound forms in such small quantities that it is impossible to collect enough for analysis. Luther made Ag_2Cl by pouring chlorine water over powdered silver, and found it was a dark violet in color.* The plate after exposure in the camera shows no trace of such coloration, and the image is said to be latent. The reduction by the light can hardly have been to metallic silver, because metallic silver is soluble in nitric acid, and the exposed plate may be bathed in dilute nitric acid without destroying the latent image.

The liberated bromine unites with gelatine, *i.e.*, one of the products of the reaction is removed, and this explains the great "rapidity" of our dry plates.

When the halogen salt is acted on by light, it may be that some of the radiant energy is converted to chemical; it may be that the light acts catalytically, only hastening a process which occurs very slowly in the dark; perhaps the action is partly one and partly the other; we are not sure. The evidence is rather in favor of the view that the light acts catalytically; for films and plates deteriorate with age, acting, after months or years, as if the reaction which occurs so rapidly upon exposure to light had been taking place slowly.

Development. The exposed plate is immersed in a reducing agent of such a strength that the parts affected by light are reduced, while the unaffected parts remain unaltered. The product of the reduction is metallic silver. It will be noticed that the result is a silver negative like that obtained by the wet plate process. But there is a difference. In the wet plate process the silver of the negative is obtained from the developer while in the dry plate process it is obtained from the silver compound in the light-sensitive emulsion. The suggestion has been made to distinguish between these two processes by calling the wet plate process a physical, the dry plate process a chemical, development; but both processes are chemical, and it is hard to see what value such distinction could possibly have.

The growth of the silver nucleus occurs only where the developer and silver bromide are both present. If a small amount of sodium

* See R. Luther, "Die Chemischen Vorgänge in der Photographie" (1899).

thiosulphate be added to the developer, it will dissolve silver bromide from one portion of the plate and transport it to the places where silver is being reduced; that is, it intensifies the effect; but if too much thiosulphate be used, silver is deposited all over the plate, or, in the language of the photographer, the plate is fogged.

Sodium sulphite is a reducing agent, and it alone will develop a plate, though slowly and incompletely. If added to another reducing agent, it enhances the action of the latter by removing oxygen from the solution.

Retarders. In case of an overexposure, the image flashes up too quickly, the whole plate is likely to receive a deposit of metallic silver, and the resulting negative will then lack contrast. We add a few drops of a concentrated solution of potassium bromide, and this retards the action of the developer, enabling us to secure the desired contrast. This is an application of the law of mass action. Development consists in the reduction of silver bromide to metallic silver, and bromide ions go into solution. Increase the concentration of the bromide ions present in the developer and this diminishes the velocity of the reaction of which they are one product. In case the sensitive salt is silver chloride, a solution of common salt will act as a retarder.

Reversal of the Image. The compound of gelatine and bromine which forms when an exposure is made is more difficultly soluble in water, and less permeable to water, than gelatine. The longer the exposure the greater this effect. If we overexpose sufficiently, the developer has such difficulty in getting into the film at the most exposed places that it acts as much on the less exposed portions. The result is a lack of contrast in the negative. Such a negative is spoken of as "flat." If the overexposure is carried far enough, the developer may act most on the least exposed parts, and give us, not a negative, but a positive. This is called reversal of the image. The time required for this effect is rather long. A plate which gave a good normal negative after an exposure of one-tenth of a second was exposed three hours and then gave a positive.

If a plate is exposed even longer than is necessary to give a reversal of the image, the whole film becomes so impermeable that the developer finds it about equally hard to enter at one place or another. Then we obtain a negative as if the exposure had been normal. These phenomena are sometimes called "solarization."

In case of overexposure, it is desirable to use a dilute developer

and to develop very slowly. Under such circumstances the developer has time to penetrate through the less permeable portions of the gelatine film. This is one of the reasons that the so-called tank development is so much more satisfactory than the other methods.

Fixing. After the silver image has reached the desired strength or intensity, there remains a good deal of unaltered silver bromide, which, if exposed to light, would undergo transformations similar to those which made the picture, and thus the negative would be spoiled. This silver bromide must be removed, and this is accomplished by soaking the negative in a solution of sodium thiosulphate, which dissolves the silver bromide, forming complex silver ions. The sodium thiosulphate solution also dissolves oxygen from the atmosphere, and carries it to the silver image, which is thereby oxidized. This oxide is soluble in sodium thiosulphate solution, therefore too long immersion in the fixing solution decreases the intensity of a negative.

Intensification. In case the negative is too weak, one of several methods for intensifying may be employed. If it is immersed in a solution of silver nitrate which contains also a reducing agent, metallic silver is deposited where silver already is present. This amounts to an additional development on the plan of the wet plate process.*

Luther† describes the following interesting experiment: A dry plate was exposed and then put directly into a solution of sodium thiosulphate. This reduced the Ag_2Br to metallic silver, and dissolved the unacted-upon silver bromide. The plate was absolutely glass-clear, for the particles of silver were too small to be seen. It was then put into a solution of silver nitrate containing a reducing agent, and metallic silver was reduced out on the nuclei which were present, though invisible, and the image appeared slowly until a useful negative was obtained.

Optical Sensitizing. It was discovered by Vogel that if a substance, itself not sensitive to light, but which will absorb certain rays, is mixed with one that is sensitive to light, the sensitiveness of the

* The fundamental principle of the intensification methods with mercury is probably correctly indicated by the following reaction:

$$3\,Ag + 2\,HgCl_2 = 2\,HgCl + Ag_2Cl + AgCl.$$

The mercurous chloride and the silver chloride then unite to form a white insoluble compound. When ammonium hydroxide is brought in contact with this, we obtain a black substance of unknown composition which contains mercurous chloride, silver chloride, and ammonia.

† *Loc. cit.*

whole is frequently much increased. This is known as optical sensitizing. The usual dry plates of photography may be dyed with various aniline dyes, and, as is well known, this makes them peculiarly sensitive to particular colors, and we have thus a variety of so-called orthochromatic plates. Besides this particular sensitiveness to certain colors, the plate as a whole is usually more " rapid " than one not so treated.

Chemical Sensitizing. It has also been found that if we add to a light-sensitive substance a second substance, capable of combining chemically with one of the products of the action of light, we can thus much increase the sensitiveness of the original substance. The fact already alluded to that gelatine unites with bromine is an instance of " chemical sensitizing " and an illustration of the wide applicability of our fundamental law of mass action and our ideas concerning chemical equilibrium; for this plan of removing one of the products is the customary method to force a reaction to proceed in the direction we wish.

Printing Processes. The methods for obtaining positive copies on paper from negatives are very numerous, and it would lead us much too far to take them up in detail, though their discussion would bring out a number of scientifically interesting facts and problems.

Most used at present are the "gaslight" papers. These are covered with a film practically the same as that on a slow plate. They are exposed for a few seconds under the negatives to artificial light and then are developed and fixed as if they were plates. The pictures thus consist of metallic silver.

We shall pass over the somewhat antiquated "gold toning" process, the always useful " blue prints," the platinum prints, and other processes. But it seems desirable to say a few words about the pigment process, because it is the most permanent and beautiful of all, and so few, even of the enthusiastic amateur photographers, seem to appreciate its possibilities and its simplicity.

The Pigment Process. Gelatine containing some potassium dichromate is sensitive to light when dry, hardly sensitive when wet. Light produces a change which makes this " chrome-gelatine " relatively insoluble. This change is due to an oxidation of the gelatine by the potassium dichromate, or possibly in a measure to a combination of the gelatine with the reduction product of the potassium dichromate, or possibly it is due to a combination of these two causes.

The action is not fully understood, and this is one of the many instances where the technique of photography has far outstripped the science.

Mix with gelatine any permanent pigment such as is used in oil painting and coat paper with this emulsion. Sensitize it shortly before exposure by immersion in a dilute solution of potassium dichromate. When dry, expose the paper to light under a negative. Where the light passes most readily, the gelatine is rendered most insoluble. The image on the negative is faithfully reproduced in terms of solubility and insolubility of the gelatine layer. After exposure, dissolve out the remaining soluble gelatine with warm water, and the picture appears in the pigment embedded in the insoluble gelatine. This is generally known as the " carbon " process because the first pigment used was finely divided carbon. As any colored pigment may be used quite as well as carbon, the range of possible effects is large.

Emission of Light. We have devoted as much space as we can spare to conversions of radiant energy into chemical energy, and must now consider, very briefly, the converse processes, the changes of chemical energy into radiant energy.

Chemical reactions are usually our sources of heat, and any substance when hot enough emits light. Thus, properly speaking, all sources of artificial light, with the exception of electric lights, might properly be considered under this subdivision. The great generalizations formulating the connection between temperature and light, Stefan's and Wien's laws, were stated in Chapter VIII.

There is no more interesting fact in the science of chemistry or physics than that the elements as gases emit characteristic spectra. This, too, was discussed in some detail in Chapter VIII, which is indeed as much a chapter on actinochemistry as this.

Luminescence. We know a number of processes which emit a light greater than corresponds (according to Stefan's law) to the temperature of the emitting body. We call these instances of " luminescence." These have been subdivided into the phenomena known as electroluminescence, thermoluminescence, triboluminescence, crystallization luminescence, fluorescence, and phosphorescence. We shall describe, very briefly, a few instances of each.

Electroluminescence. Rarefied gases under the influence of a rapidly alternating high-potential current become luminous and emit light of an intensity much greater than corresponds to their tempera-

ture. We must let what was said regarding this phenomenon in Chapter VIII suffice.

Thermoluminescence. While all bodies begin to emit a dull-red light at about 525°, and Stefan's law begins to apply more or less well, we know of a few substances which begin to emit light, and of shorter wave length, at lower temperatures. Diamond, marble, and fluorite are instances. Some samples of fluorite emit visible light in a bath of melted paraffin. This is the phenomenon known as thermoluminescence.

Triboluminescence. By derivation this term indicates the giving out of light due to friction. If a bottle containing crystals of uranium nitrate is shaken vigorously in the dark, flashes of light are seen. The same phenomenon, but less brilliant, may be observed when crystals of sugar are crushed. Over a hundred different crystalline substances have been found to show this "triboluminescence." It seems to have some connection with the crystalline structure, but we do not know what.

Crystallization Luminescence. When arsenious acid, or sodium fluoride or sulphide, and some other substances, crystallize out of saturated solutions, flashes are sometimes seen. Perhaps a flash accompanies the formation of each crystal, and only a few of these are intense enough to be visible. It is altogether probable that the cause of this, whatever it may be, is the same as the cause of triboluminescence, whatever that may be.

Fluorescence. A substance is said to fluoresce if, when radiant energy impinges upon it, it sends out a light of its own different from that impinging. It was so called because the phenomenon is particularly marked with some samples of fluorite (CaF_2).

When X-rays or rays from radium strike a surface covered with zinc sulphide or barium platinocyanide, these substances emit visible light; they fluoresce, as described in Chapter X. Neither substance has this property when in solution. Diamonds, rubies, and many other substances, if mounted within a Crookes's tube in the path of cathode rays, emit light (fluoresce) with a brilliance truly spectacular.

Light from the sun, an arc light, or other rather intense source causes fluorescence in many liquids and solutions. Doubtless most of us have noticed the characteristic greenish light about the meniscus of mineral oils, and have seen the phenomenon in solutions of fluorescein, eosin, and other organic dyes. A solution of sulphate of

quinine fluoresces with a bluish light, a solution of chlorophyll with a dark-red light, a solution of litmus with a brownish light. Faint traces of fluorescence have been detected upon an extraordinary assortment of objects, — white paper, cork, bones, wood, and many samples of colorless glass.

Stokes's Law. For many years it was thought that in all cases the rays sent out from a fluorescent body were of greater wave length than that of the rays causing the fluorescence. This was known as Stokes's law. But recent investigations have proved that in many cases it does not hold.

We are very much in the dark as to the cause of fluorescence. Evidently enough, the fluorescing body absorbs radiant energy of definite wave lengths and alters these wave lengths, but what the mechanism is whereby this change is consummated we do not know. The suggestion has been made that the phenomenon is intimately connected with tautomerism; that the light converts one molecular structure into a tautomeric form, and that the change back is accompanied by the emission of light of a different wave length from that absorbed. It has also been suggested that the light moves some atoms out of their normal position in a molecule, and that when these "spring" back into place the movement is accompanied by the luminescence. There is no proving nor disproving such hypotheses.*

Phosphorescence. Sulphides of calcium, barium, and strontium, after being exposed to an intense light for some time, emit light for several hours. Curiously enough, the chemically pure substances will not do this. Traces of manganese, copper, or bismuth present as impurities appear to be essential. These substances form the basis of the familiar luminous paints. Other salts of the alkaline earth metals and a few gems and minerals possess this property in less degree. An ingenious apparatus was devised by E. Becquerel to detect feeble phosphorescence. The substance to be investigated is placed between revolving disks with holes in them. These holes are so arranged that the object is first exposed to a bright light; then this light is entirely cut off and while the object is in total darkness the observer looks at it through another hole. If he sees anything the object must be "phosphorescing." By measuring the rate at which the disks revolve it is possible to calculate how long the object phospho-

* For an extensive list of fluorescent substances see H. Kauffmann, "Die Beziehungen zwischen Fluoreszenz und chemischer Konstitution"; Ahren's "Sammlung chemischer und chemisch-technischer Vorträge," Vol. II, pp. 1–102 (1907).

resces. This apparatus has greatly extended the list of substances known to possess this property.

The temperature exercises a marked effect. In all cases it alters the color (wave length) of the light given out. Becquerel found that the higher the temperature the greater the wave length of the phosphorescence from strontium sulphide; but in most cases the reverse is the fact, and the higher the temperature the shorter the wave length.

After the phosphorescence of calcium sulphide has died out, upon raising the temperature it begins again. But if the temperature is raised to 400° the property is entirely lost.

The sulphides of calcium and strontium cease to phosphoresce at −80°, but at the temperature of liquid air (−180°) a most miscellaneous assortment of articles acquires the property. Acetophenone, urea, salicylic acid, starch, celluloid, glue, leather, egg shells, and feathers are in this list.

Again we are at a loss to " explain " the phenomenon. We can do no more than make the self-evident statement that the exciting light must produce a chemical reaction which proceeds in the opposite direction in the dark with the emission of light.

Phosphorescence without Previous Illumination. Moist phosphorus, in contact with the air, emits a glow, and from this phenomenon originated the name phosphorescence. No previous illumination is required, and the source of this radiant energy must be the slow oxidation. It is an interesting fact that if the partial pressure of the oxygen is too great no glow is seen. Moist phosphorus in pure oxygen at atmospheric pressure does not phosphoresce.

A number of cases are known where a chemical reaction is accompanied by luminescence, and the term chemiluminescence is applied to them; but, after all, this term might be applied to both fluorescence and phosphorescence and such extensive subdivision is rather pointless. Mix 35 cm.^{3} of a 50 per cent solution of potassium carbonate, 35 cm.^{3} of a 10 per cent solution of pyrogallol, and 35 cm.^{3} of a 35 per cent solution of formaldehyde. To this mixture add rapidly 50 cm.^{3} of a 30 per cent solution of hydrogen peroxide. Vigorous foaming ensues, accompanied by a reddish glow.*

Physiological Phosphorescence. A number of insects and infusoria emit visible light in the dark. The "firefly" is often quoted as the most efficient light producer known to us. It is assumed that

* This experiment and a number of others are described by M. Trautz *Zeitschr. f. Elektrochem.*, 10, 593–6 (1904).

all energy is converted to light without loss by this insect. The phosphorescence in the ocean emanates from infusoria. Some tropical plants are said to phosphoresce. In general the phenomenon of " physiological phosphorescence " is more frequent in the tropics than in colder climates.

Decaying wood sometimes shows phosphorescence. This has been traced to the presence of lower organisms. A species of bacteria which thrives on old potatoes is brightly luminous. Decaying animal matter of many kinds—meat, cheese, and particularly salt-water fish—phosphoresce. Some of these instances were attributed to the production of phosphine, but this theory failed to withstand close investigation. Probably lower forms of life are almost always responsible.

Why these particular life processes should be accompanied by the emission of light we have no idea. We know that the presence of oxygen is essential in all cases, and so can say it is the result of slow oxidation. Many patient investigations have been undertaken, but have not yet taught us how to reproduce the effect in the laboratory.

The whole subject of actinochemistry is of peculiar interest and importance, for the transformation of a small fraction of one per cent of the radiant energy from the sun furnishes us with food, light, and heat, our prime necessities. If we could learn to transform but a little fraction more into these useful forms, or to hasten only a little the reactions going on all about us, it would greatly increase the wealth of mankind. The source of all wealth is the knowledge which gives us power to direct and govern the processes of nature.

APPENDIX

A METHOD FOR CALCULATING CHANGES IN GASEOUS VOLUMES

CONVERT temperatures on any other scale into temperatures on the absolute scale and apply first one gas law and then the other. This is preferable to the use of formulæ which are easily forgotten.

100 cm.^{3} of a gas at 18° and under a pressure of 740 mm. will occupy what volume under normal conditions?

SOLUTION

	v	t	T	p
Initial conditions.....	100	18°	291°	740
Final conditions.....	x	0°	273°	760

Ask yourself whether the change in temperature will increase or diminish the volume, and multiply the initial volume by the fraction obtained by putting one absolute temperature in the numerator and the other in the denominator, *in such a way as to produce the effect indicated by the law.* In this example a change from 291° to 273°, being a diminution in temperature, must be accompanied by a corresponding diminution in volume. Therefore, the 100 cm.^{3} must be multiplied by $\frac{273}{291}$.

Ask yourself whether the change in pressure will increase or diminish the volume, and multiply by the fraction obtained by putting one pressure in the numerator and the other in the denominator, *in such a way as to produce the effect indicated by the law.* In this example a change from 740 mm. to 760 mm., being an increase in pressure, must be accompanied by a diminution in volume. Therefore, the $100 \times \frac{273}{291}$ must be multiplied by $\frac{740}{760}$. Working out the expression, $100 \times \frac{273}{291} \times \frac{740}{760}$, gives the answer.

250 cm.^{3} of a gas at $-$ 20° and under a pressure of 755 mm. occupies what volume at $+$10°, under a pressure of 730 mm.?

SOLUTION

	v	T	p
Initial conditions.....	250	253°	755
Final conditions.....	x	283°	730

The temperature is increased, therefore the volume is increased, and we must multiply by $\frac{283}{253}$. The pressure is diminished, therefore the volume is increased, and we must multiply by $\frac{755}{730}$.

$$x = 250 \times \frac{283}{253} \times \frac{755}{730} = \text{volume sought.}$$

USE OF LOGARITHMS

It may appear strange to give directions for the use of logarithms even in the appendix of a book such as this. But it is stranger how many students, when first required to do a problem involving the gas laws, set about it by the painfully tedious processes of long division and multiplication. Questioned, they acknowledge a dim recollection of logarithms, but confess they are unable to use the tables. The following brief summary is therefore given, to save the time of both teacher and students.

In any system of logarithms some positive number is selected as a base, and then all other numbers are regarded as powers of this base. If $a^x = b$, then x is the logarithm of b in the system of which a is the base.

Two systems are in constant use: the natural, or Napierian system, of which the base is 2.718 281 828 4 . . . , a value denoted by e, selected for reasons into which we shall not enter; and the Briggs, denary, or decimal system, of which the base is 10. Natural logarithms are denoted by the symbol ln, Briggs logarithms by the symbol log. The relationship between the logarithms in the two systems is: $0.434\,29\ ln\, x = \log x$, or $2.3026 \log x = ln\, x$.

Briggs logarithms are used almost exclusively in the calculations of physical chemistry. They consist generally of two parts: an integral part, to the left of the decimal point, called the characteristic; and a fractional part, to the right of the decimal point, called the mantissa.

Their use much abbreviates calculations because of the following four facts:

First. The logarithm of the product of two or more positive numbers is the sum of the logarithms of the numbers.

Second. The logarithm of the quotient of two positive numbers is obtained by subtracting the logarithm of the divisor from the logarithm of the dividend.

Third. The logarithm of a power of a positive number is found by multiplying the logarithm of the number by the exponent of the power.

Fourth. The logarithm of the root of a positive number is obtained by dividing the logarithm of the number by the index of the root.

To obtain the logarithm of a number, first look up the mantissa in the tables. For instance, suppose the logarithm of 745 is wanted and we have a "four-place" table. Follow down the left-hand vertical column until the number 74 is found, and then follow the horizontal to the column headed 5. This gives the mantissa .8722.

A simple rule to find the characteristic is the following: If one figure of the original number stands to the left of the decimal point, the characteristic is 0; if two, the characteristic is 1; if three, the characteristic is 2, and so on. Three figures stand to the left of the decimal in 745, and so the characteristic is 2 and the whole logarithm is 2.8722.

Suppose the number whose logarithm we want is 7453. We find from the tables the mantissa is more than .8722 and less than .8727. It is three-tenths of the way on from the smaller to the larger mantissa. The difference is 5, and three-tenths of 5 is $1\frac{1}{2}$. Four-place tables serve only to furnish close approximations to the right answers, and so we neglect the half and call the mantissa .8723. Most tables have columns containing proportional parts which facilitate this interpolation. The characteristic of our number is 3, and so the logarithm is 3.8723.

A convenient rule for determining the characteristic of decimal fractions is to imagine a decimal just to the right of the first significant figure and then count figures until the decimal is reached. The number thus counted is the characteristic, and it has a minus sign, which is conveniently written over it. Thus the characteristic of 0.003 42 is $\bar{3}$, the whole logarithm being $\bar{3}$.5340. The logarithm of 0.237 is $\bar{1}$.3747, etc. If, in adding logarithms, there is something to be carried to the left of the decimal, it is added to the sum of the

characteristics. Remember that adding a positive value diminishes a negative value. Thus $\bar{3}.5340 + 1.6231 = \bar{1}.1571$. If, in subtracting logarithms, the mantissa subtracted is greater than the mantissa from which it is subtracted, the sum of the characteristics is diminished by 1. Thus, $\bar{3}.5340 - 0.6231 = \bar{4}.9109$.

A gas occupied 242.7 cm.^{3} at 733 mm. and at 17°. We wish to know its volume at 760 mm. and 0°. We have: $x = 242.7 \times \frac{733}{760} \times \frac{273}{290}$.

$$\begin{array}{rlrl} \log 242.7 &= 2.3850 & \log 760. &= 2.8808 \\ \log 733. &= 2.8651 & \log 290. &= \underline{2.4624} \\ \log 273. &= \underline{2.4362} & & 5.3432 \\ & 7.6863 & & \\ & \underline{5.3432} & & \\ & 2.3431 = \log \text{ of answer.} & & \end{array}$$

Look up this mantissa in the table and write the number corresponding to it (2203) without regard to the decimal. To have the characteristic 2, there must be three numbers to the left of the decimal, therefore the answer is 220.3.

Find the third power of 63.7.

$$\begin{array}{rl} \log 63.7 &= 1.8041 \\ & \underline{\quad\quad 3} \\ & 5.4123 \end{array}$$

This logarithm we find from the tables corresponds to the number 258 400, which is a close approximation to the answer. If a closer approximation is desired, five- or six-place logarithm tables must be used.

Find the cube root of 63.7. $\log 63.7 = 1.8041$. Divide this by 3 and we get 0.6014. This logarithm corresponds to the number 3.994, which is then a close approximation to the answer.

Find the cube root of 0.064. $\log 0.064 = \bar{2}.8062$. Here it is convenient to rewrite the logarithm: $2.8062 = 8.8062 - 10$.

$$\begin{array}{l} 3)\underline{8.8062 - 10} \\ \quad 2.9354 - \quad 3.3333 \\ \quad \underline{3.3333} \\ \quad \bar{1}.6021 \end{array}$$

and this logarithm corresponds to the number 0.400, which is the answer.

THE USE OF EXPONENTS

ONE more thing students often seem to have forgotten by the time they undertake the study of physical chemistry is the use of exponents to denote very large or very small values. The following brief statement will serve as a reminder:

$$10^2 = 100; \quad 10^6 = 1\,000\,000, \text{ etc.}$$
$$10^1 = 10; \quad 10^0 = 1; \quad 10^{-1} = 0.1;$$
$$10^{-6} = 0.000\,001 = \frac{1}{1\,000\,000} = \frac{1}{10^6}.$$

By using minus exponents we may write a fractional expression on one line. For instance, velocity is a distance divided by a time; velocity $= \frac{\text{cm.}}{\text{sec.}}$. We may write, velocity $= \text{sec.}^{-1}\,\text{cm.}$

$$a^m \times a^n = a^{m+n} \qquad \sqrt[n]{\sqrt[m]{a}} = \sqrt[mn]{a} \qquad a^{\frac{1}{n}} = \sqrt[n]{a}$$

$$\frac{a^m}{a^n} = a^{m-n} \qquad (\sqrt[n]{a})^m = \sqrt[n]{a^m} \qquad a^{\frac{m}{n}} = \sqrt[n]{a^m}$$

$$(a^m)^n = a^{mn} \qquad a^{-m} = \frac{1}{a^m} \qquad \frac{\sqrt[n]{a}}{\sqrt[n]{b}} = \sqrt[n]{\frac{a}{b}}.$$

$$\sqrt[n]{a}\,\sqrt[n]{b} = \sqrt[n]{ab}$$

$$(a+b)(a-b) = a^2 - b^2.$$
$$(a+b)^2 = a^2 + 2ab + b^2.$$
$$(a-b)^2 = a^2 - 2ab + b^2.$$
$$(a+b)^3 = a^3 + 3a^2b + 3ab^2 + b^3.$$
$$(a-b)^3 = a^3 - 3a^2b + 3ab^2 - b^3.$$

METRIC SYSTEM AND SOME EQUIVALENTS

Meters.		
10 000	Myriameter	6.2137 miles.
1 000	Kilometer	0.621 37 mile.
100	Hectometer	328 feet 1 inch.
10	Dekameter	393.7 inches.
1	Meter	39.37 inches.
0.1	Decimeter	3.937 inches.
0.01	Centimeter	0.3937 inch.
0.001	Millimeter	0.039 37 inch.
0.000 001	Micron	0.000 039 37 inch.

10,000 square meters	Hectare	2.471 acres.
100 square meters	Are	119.6 square yards.
1 square meter	Centare	1550 square inches.

Liters.		Dry measure.	Liquid measure.
1000	Kiloliter or stere,	1.308 cubic yards	264.1700 gallons.
100	Hectoliter	2 bushels and 3.35 pecks	26.4170 gallons.
10	Dekaliter	9.08 quarts	2.6417 gallons.
1	Liter	0.908 quart	1.0567 quarts.
0.1	Deciliter	6.1022 cubic inches	0.8450 gill.
0.01	Centiliter	0.6102 cubic inch	0.3380 fluid ounce.
0.001	Milliliter (cm.^{3})	0.0610 cubic inch	0.2700 fluid drachm.

Grams.		Volume of water which at 4° has this weight.	Avoirdupois measure.
1 000 000	Millier or tonneau	1 cubic meter	2204.6 pounds.
100 000	Quintal	1 hectoliter	220.46 pounds.
10 000	Myriagram	10 liters	22.046 pounds.
1 000	Kilogram	1 liter	2.2046 pounds.
100	Hectogram	100 cubic centimeters	3.5274 ounces.
10	Dekagram		0.3527 ounce.
1	Gram	1 cubic centimeter	15.4320 grains.
0.1	Decigram		1.5432 grains.
0.01	Centigram		0.154 32 grain.
0.001	Milligram	1 cubic millimeter	0.015 43 grain.

MISCELLANEOUS DATA AND FORMULÆ

1 pound avoirdupois	453.6	grams.
1 ounce avoirdupois	28.35	grams.
1 grain avoirdupois	0.0648	grams.

One cubic foot of water = 6.24 gallons; at 16.6° C. weighs 62.24 lbs.

One horse power = 33 000 foot-pounds per minute = 746 watts.

$\pi = 3.141\,59$.

Let the radius of a circle $= r$ and its diameter $= D$. Then $D = 2r$; the circumference $= 2\pi r$; the area $= 2\pi r^2$.

Let the radius of a sphere $= r$. Then the surface area $= 4\pi r^2$ and the volume $= \frac{4}{3}\pi r^3$.

Area of a triangle with base b and height $h = \frac{1}{2}bh$.

INDEX

(Proper names are in italics.)

ABBÉ refractometer, 190.
Abnormal osmotic pressure, 220.
  vapor densities, 170.
Absolute measures, 19, 21.
  temperature scale, 34.
  zero, 33, 138.
Absorption bands, 105.
  Bunsen's coefficient of, 332.
  of rays, 129.
  of X-rays, 114.
  photochemical, 504.
Acceleration, 19.
Accumulators, *see* Storage cells.
Acids, affinity constants of, 388.
  basicity of, 460.
  dissociation constants of, 385.
  division of a base between, 386.
  strength of, 72, 385.
Actinium, 123.
Actinochemistry, 24, 502 *et seq.*
Actinometer, 506.
  electrochemical, 508.
  mercuric oxalate, 507.
  silver chloride, 507.
Action of light in photography, 511.
Additive properties, 194.
Adhesion, 75.
Adiabatic expansions, 255.
Adsorption, heat evolved during, 241.
  of dissolved substances, 241.
  of gases, 240.
  of liquids, 241.
"Advanced" subjects, 38.
Affinity, chemical, 13, 68 *et seq.*, 77.
  tables, 69.
Affinity constants, in other solvents than water, 388.
  of acids (table), 387.
  of bases (table), 388.
Agglutination, 248.
Aggregation, conditions of, 32.
Air, liquefaction of, 258 *et seq.*
Albertus Magnus, 70.
Alchemists' views, 69.
Allotropic forms, energy contents of, 413.
Allotropy, 83.
Alloys, 239.
Alpha rays, 123, 124.
Amagat, 156.
Amalgam electrodes, 479.
Amicrons, 252.
Ammeter, 425.
Amonton, 32, 139.
Amorphous solids, 37, 196.
Ampere, A. M., 426.
Ampere, 426.
Amperemeter, 425.
Ampere's rule, 425.
Amphoteric electrolytes, 448.
Analysis, electrochemical, 489.
  of water, 59.
  sugar, 230.
Andrews' isotherms, 154, 260.
Andrews, Thomas, 154, 262.
Ångström units, 99.
Anions, 222, 223, 431.
Anisotropic substances, 200.
Anode, 431.
Anode rays (canal rays), 115, 124.
  nature of, 119.
Apparent mass, 130 *et seq.*
Approximations, 11.
Archimedes spiral, 96.
Areometer, 175.
Argon, discovery of, 22.
  group, 92.
Aristotle, 56.
Armstrong, 273.
Arrhenius, S., 188, 221, 389, 436, 503.
Arrows, use of, 43.
Artificiality of classifications, 37.
d'Arsonval galvanometer, 425.
Association, and freezing point, 326.
  inferences regarding, 375.
  in liquids, 179, 180, 185.
Aston, 185.
Astrophysics, *see* Stellar chemistry.
Asymmetric, atoms, 233, 234.
  molecules, 234.
Atom, 56, 57, 61, 62, 109, 132.
Atomic heat, 65.

Atomic, refraction, 194, 195.
theory, 41, 56 *et seq.*
volume, 92.
of liquids, 177 *et seq.*
weight, 41, 43, 57, 195.
selection of, 42 *et seq.*
table, 54.
Atomicity, 58.
Atoms, in fixed positions, 84.
not ultimates, 120.
Attraction hypothesis (regarding osmosis), 216.
Attributes, 17.
Austen, Roberts, 239.
Autocatalysis, 368.
Available energy, 27.
Avogadro's theory, 11, 62, 135, 150, 157.
applied to solutions, 221.
deduction of, 141.
Axes, crystal, 197.
optical, 201.

BALANCED action, 277, 373.
Baly, E. C. C., 103.
Bancroft, W. D., 296, 484.
Barlow, W., 203.
Barnes, 36, 405.
Bartell, F. E., 219.
Base, division of, between two acids, 386.
Bases, affinity constants of, 388.
Basicity of acids, 460.
Batteries, gravity, 473.
primary and secondary, 472.
storage, efficiency of, 497.
see also Cells.
Baume, G., 157.
Bayley, R. C., 509.
Baynes, 156.
Beckmann, 317.
Beckmann thermometer, 314, 408.
table of corrections for, 317.
Becquerel, A. C., 508.
Becquerel, A. E., 517, 518.
Becquerel, A. H., 121.
Behrens, H., 197.
Belief, 15.
Belloc, 238.
Benedicks, C., 240.
Benzene ring, 58.
Bergmann, T. O., 71, 75.
Berkeley, Earl of, 212.
Bernoulli, D., 135.
Berthelot, D., 157.
Berthelot, P. E. M., 73, 238, 379, 404, 407, 420, 421.
Berthollet, C. L., 59, 71, 75, 352, 353, 355, 506.
Berzelius, J. J., 59, 60, 73, 366.
Beta rays, 123, 124.
Bigelow, S. L., 219, 244, 316, 369.
Biltz, H., 159.
Bimolecular reactions, 358.
Binary electrolytes, 388.
Biot, J. B., 231.
Birotation, 229.
Bivariant system, 291.
"Black body," 101.
Bleier and Kohn (or Lumsden) method, 167 *et seq.*
Boerhaave, H., 70, 71.
Boiling point, 23, 279 *et seq.*
and critical temperature, 283.
below melting point, 287.
constancy of, 280.
corrections to, 281.
determination of, 281.
graphical representation of, 280.
raising of, and vapor pressure, 312.
regularities in, 282.
Boiling-point method, 315 *et seq.*
as measure of dissociation, 322.
formula, 313.
de Boisbaudran, L., 103.
Bodenstein, M., 376, 377.
Bolometer, 101.
Boltwood, B. B., 124.
Boltzmann, 136, 141.
Bomb calorimeter, 407.
"Bonds," 85.
Boscovich, 133.
Bott, 167.
Boyle, Robert, 32, 56, 69.
Boyle's law, 12, 32.
applied to solutions, 212.
deduction of, 140.
Branching circuit, calculating current in, 429.
Bredig, G., 250, 367, 368, 421, 448.
Bridge, Wheatstone, 429.
British thermal unit, 405.
Brownian movement, 146, 216, 252.
Brown, Robert, 146.
Buffon, 75.
Bunsen, R. W., 103, 332, 407, 506, 507.
Bunsen's, coefficient of absorption, 332.
molecular weight method, 142.
Burgess, C. H., 507.
Burning limestone, 399.

CADMIUM standard cell, 468.
Cailletet, 255.
Calcium carbonate, dissociation of, 399.
Calculation, of degree of dissociation of gases, 172.
of quantities present at equilibrium, 380.

Calibration of wheatstone bridge wire, 430.
Callendar, 36, 405.
Calomel electrode, 481 *et seq.*
Calorie, small, large, average, 35, 404, 405.
Calorimeter, 149, 405 *et seq.*
bomb, ice, steam, 407.
water, 406.
Canal rays (anode rays), 115, 124.
Capacity factor, of cell, 439.
of chemical energy, 77 *et seq.*
Capacity for chemical combination, 78 *et seq.*
indicating, 81.
Capacity, specific induction, 463.
Capillary, constant, 181 *et seq.*
electrometer, 469.
phenomena, 181 *et seq.*
structure of osmotic membranes, 219.
structure of solutions, 220.
Carbon monoxide poisoning, 105.
Carbon process, 515.
Carnot, Sadi, 26.
Carrara, G., 462, 464.
Carriers of energy, 28, 112, 132.
Catalysis, 365 *et seq.*
and equilibrium, 403.
negative, 369.
Catalytic effect, and concentration of catalyzer, 367.
of light, 505.
of metals, 241.
Cataphoresis, 252, 455.
Cathode, 431.
Cathode rays, 103, 114, 124.
nature of, 115 *et seq.*
Cations, 222, 223, 431.
Cause, 13.
Cell, capacity factor of, 439.
"chloride," 495.
concentration, 473.
for conductivity method, 437.
in general upon, 473.
lead-sulphuric acid, 494.
nickel-iron-alkali, 500.
reversible and nonreversible, 473.
standard, 468.
storage, 494.
temperature coefficient of, 491.
voltaic, galvanic, 473.
Celsius scale, 33.
Centigrade scale, 33.
Cermak, P., 127.
Chalcolite, 122.
de Chancourtois, B., 89.
Chapman, D. L., 507.
Charge, on a corpuscle, 117, 118.
on an ion, 222.
Charles' law, 32.
Chemical action at low temperatures, 140.
Chemical affinity, 13, 77.
Chemical compound, 39, 40.
Chemical dynamics, 352.
Chemical energy, 23, 68 *et seq*, 83.
capacity factor of, 77.
division of, into factors, 76, 80.
intensity factor of, 76.
Chemical energy, and electrical energy, 490.
and radiant energy, 507.
Chemical equilibrium, 71, 265, 371 *et seq.*
in heterogeneous systems, 393.
Chemical kinetics, mechanics, 352.
Chemical notation, 39.
Chemical philosophy, 4.
Chemical potential, 77.
Chemical processes, 23.
Chemical reactions, all reversible 372.
equilibrium in, 371 *et seq.*
velocity of, 352 *et seq.*
Chemical sensitizing, 514.
Chemical statics, 352.
"Chloride" cells, 495.
Ciamician, G., 506.
Circularly polarized light, 201.
Clapeyron-Clausius formula, 302.
Clark standard cell, 469.
Classification, may be overdone, 374.
of crystals, 197.
of energies, 23.
of organic chemistry, 85.
of solutions, 206.
Classifications are artificial, 37.
Clausius, 136, 151.
Clausius-Clapeyron formula, 302.
Clement, 366.
Clerk-Maxwell, see Maxwell.
Clifford, W. K., 16.
Clouds, formation of, 269.
Coagulation, 247.
Coefficient, absorption (table), 332, 333.
distribution or partition, 350.
economic, 301.
isotonic, 220.
of solubility, 332.
Coefficient, temperature, of a cell, 491.
of processes, 304.
of standard cells, 469.
Cohesion, 75, 83.
Cohesion, specific, 182.
Colligative properties, 213.
Collins, E., 434.
Collodion, membranes, 244.
process, 509.

Colloidal particles, size of, 251.
Colloidal solutions, 37, 243 *et seq.*
of metals, Bredig's method, 250.
Colloids, 243.
protecting, 248.
Color of ions, 384.
Combining capacity, 78 *et seq.*
Combining gas laws to one expression, 34.
Combining volumes, law of, 41.
use in selecting symbol weights, 47 *et seq.*
Combining weights, 40, 43.
Combustion, heat of, 408.
spontaneous, 365.
Comparison of measurements, 147.
Compensation method, Poggendorff's, 467.
Compensation within the molecule, 234.
Complete equilibrium, 270.
Complex ions, 396, 447.
dissociation of, 397.
Component, 265 *et seq.*
and order of equilibrium, 373.
Compressed seconds, 20.
Compressibility of liquids, 180.
Compression, isothermal, 262.
Concentration, 207.
cells, 473, 478.
critical, 257.
of a solid is a constant, 400.
Condensed system, 292.
Conditions, corresponding, 177, 272.
reduced equation of, 273.
Conditions of aggregation, 32.
indicating, in energy equations, 410.
Conductance, 429.
specific, 438.
Conduction, effected by individual ions (table), 450.
mechanism of, 436.
of heat by gases, 147.
of heat by dissociated gases, 174.
Conductivity, equivalent (table), 441.
for heat and electricity, 93.
method, 437.
molecular, 439.
of fused and solid salts, 464.
of nonaqueous solutions, 462.
Conductors and nonconductors, 431.
Conservation, of energy, law of, 25.
of mass, law of, 29.
Constant boiling-point mixtures, 308.
Constant, dielectric, 463.
the dissociation, 378.
Constant heat summation, law of, 408.
Constants, affinity (table), 387.
critical, 258.
dissociation (table), 385.
Constants, van der Waals', 157, 158.
Constituents, ultimate, 39.
Constitution, and the dissociation constant, 456 *et seq.*
and viscosity, 188.
Constitutive properties, 84.
Continuity, 56 *et seq.*
principle of, 37.
Conventions in formulæ, 85.
Copper ferrocyanide membranes, 209.
Copper, refining, 490.
Copper sulphate hydrates, 400.
Corpuscles, charged, 109.
Corrections, van der Waals', 155 *et seq.*
Corresponding conditions, 177, 272.
Coulomb, C. A., 186, 426.
Coulomb, the, 426.
Coulometers, 433 *et seq.*
Counting ions, 118, 119.
Covolume, 179.
of solids, 205.
Critical concentration, 257.
constants, 258, 271.
density, 257.
point of solubility, 334.
pressure, 256.
temperature, 183, 255, 256.
temperature and boiling point, 283.
Crookes, Sir William, 96, 97, 103, 113.
Crookes tubes, 103, 113.
Cryohydrates, 343, 345.
Cryohydric points, 342, 349.
Crystal forms, inferences from, 203.
Crystal systems, Weiss', 197.
Crystalline, liquids, 204.
solids, 37, 196.
Crystallization, luminescence, 516.
water of, 400.
Crystalloids, 243.
Crystallography, 197 *et seq.*
Crystals, liquid, 204.
in polarized light, 202.
properties of, 199 *et seq.*
Curie, P. and Mme., 103.
Curie, Mme. P., 113, 122, 123, 124, 125.
Current density, 434.
Current, direction of, 431.
residual, 488.
Curve of atomic volumes, 93.
of density, 93.
of melting points, 93.
Cycle, 298.

Daguerre, 509.
Daguerre's process, 509.
Dalton, John, 4, 33, 40, 41, 57, 59, 61, 72.
Dalton's extension of Henry's law, 333.
Daniell cell, 473.
Dark stars, 105.

Debierne, A., 123, 125.
Decomposition potentials, 486 *et seq.*
Deduction, 15.
Definite and multiple proportions by weight, law of, 40.
Degree of dissociation, 442.
of acetic acid (table), 451.
of gases, 172.
Degrees of freedom, 267.
Delta rays, 128.
Densities, vapor, 159 *et seq.*
Density, 31.
change of with cooling, 140.
critical, 257.
current, 434.
curve of, 93.
of luminiferous ether, 111.
of liquids, 175.
Derr, L., 509.
Desormes, 366.
Determining order of a reaction, 361.
Development, photographic, 511.
Deville, H. Ste. C., 170, 401.
Dew, 269.
Dewar, Sir James, 139, 240, 258.
Dewar flasks, 259.
Dextrogyratory, 229.
Dialysis, 243.
Diameters, probable, of molecules, 144.
Dichroism, 249.
Dielectric constant, 463.
Differences of state, 83.
Diffusion, as method for molecular weights, 214.
fractional, 142.
in solids, 238.
of gases, 136.
of solutes, 208.
through hydrogels, 246.
through jellies, 214.
velocity of, 142.
Dilatometer, 292.
Dilute solutions, 207, 410.
Dilution and molecular conductivity, 440.
heat of, 408.
"infinite," 440.
Dilution law, Ostwald's, 383, 455.
Dimensions, 18.
Dimorphous substance, 199.
Direction of current, 431.
"Direction of preference," 86.
Discontinuity, 56 *et seq.*
Disintegration, end product of, 128.
Dispersed system, 246.
Dispersion, 99.
rotary, 226.
Dissociated, elements, 107.
gases, conduction of heat by, 174.
Dissociation, and explosives, 174.
and lighting, 173.
and lowering of freezing point, 326.
as explanation of constant heat of neutralization, 419.
as explanation of thermoneutrality, 418.
calculation of dilution for a definite, 458.
degree of, 442, 451.
effect on equilibrium, 378.
inferences regarding, 375.
measurement by boiling point method, 322.
measurement by conductivity method, 437.
Dissociation of calcium carbonate, 399.
of complex ions, 397.
of gases, 170 *et seq.*
of iron, 108.
of water, 461.
pressure, 398.
Dissociation constants, 378.
and chemical constitution, 456 *et seq.*
and Ostwald's dilution law, 455.
table of, 385.
Dissociation theory, argument for, 451.
compared with atomic theory, 221, 224.
Distillation, fractional, 308.
with steam, 333.
Distribution coefficient, 350.
Divariant system, 291.
Division of a base between two acids, 386.
Division of chemical energy into factors, 76.
Doebereiner, J. W., 88.
Doebereiner's triads, 88, 92.
Dolezalek, F., 494, 500.
Donnan, 362.
Doppler effect, 104.
"Double bond," 178.
Double-layer theory, 471 *et seq*, 479.
Double refraction, 200.
Double salts, 238.
Double stars, 104.
Draper, 506.
Dropping electrode, 480.
Drucker, 423.
Dry batteries, 246.
Dry plate process, 510.
Dry plates, 246.
Dualistic system, 73 *et seq.*
Dubrunfaut, 244.
Dulong, P. L., 64.
Dulong and Petit's law, 47, 64 *et seq.*
Dumas, J. B., 4, 58, 87, 89.
Dumas method, 160 *et seq.*

Dutrochet, 209.
Dyed fibers, 239.
Dynamic method for measuring vapor pressure, 281.
Dynamics, chemical, 352.
Dynamides, 130.
Dyne, 30.
Dyson, G., 167.

EBULLITION, 279.
Economic coefficient, 301.
Eder, J. M., 506, 509.
Edison cell, 500.
Efficiency of storage batteries, 497.
Efflorescence, 401.
Elasticity of molecules, 137.
of solids, 196.
Elective attractions, 71.
Electrical, analogy, 73.
endosmosis, 454.
Electrical energy, 423.
and chemical energy, 490.
converting heat directly to, 493.
factors of, 425.
Electricity, 423.
unit quantity of, 433.
wave lengths of, 100.
Electrochemical, actinometer, 508.
series, 73, 482 *et seq.*
Electrochemistry, 24, 423 *et seq.*
Electrode, amalgam, gas, 479.
calomel, 481.
dropping, hydrogen, normal, zero, 480.
potential at an, 475.
Electroluminescence, 515.
Electrolysis, 431.
Electrolytes, 222.
amphoteric, 448.
measuring resistance of, 430.
Electrolytic dissociation theory, 221 *et seq*, 436 *et seq.*
Electromagnetic, rotation, 235.
theory, 110.
Electrometer, capillary, 469.
Electromotive force, 426, 427.
calculation of, 478, 489.
measurement of, 466 *et seq.*
of lead storage cell (table), 496.
Electromotive series (table), 482 *et seq.*
Electron, 132, 200.
Electrons and ions in solution, 222.
Electron theory, 88, 112, 113, 424.
utility of, 132.
Electroscope, 121.
Electrostenolysis, 455.
"Elementary" subjects, 38.
Elements, 39, 121.
are complicated compounds, 109.
Elements, changing, 125.
isomorphism of, 199.
stability of, 129.
Elliptically polarized light, 201.
Emission of light, 515.
Empirical, formulæ, 53.
knowledge, 8.
Emulsion, 37.
Enantiomorphous forms, 232.
Enantiotropy, 296.
Endosmosis, 209.
electrical, 454.
Endothermic compounds, increasing the yield of, 403.
End product of disintegration, 128.
Energy, 21 *et seq.*
available, 27.
carriers of, 28.
classification of, 23.
conservation of, 25.
electrical and chemical, 490.
equations, 409 *et seq.*
factors of heat, 404.
free, 27.
potential, 23.
radiant, 502.
table of and factors, 25.
total, 26.
view, 112, 147.
Enzymes, 368.
Eötvös, 185.
Equation, Helmholtz', 492.
of conditions, 273.
Equations, 41, 43.
energy, 409.
Equilibrium, 264 *et seq.*
and catalysis, 403.
between calcium carbonate, lime and carbon dioxide, 399.
between gas and solution, 375.
between oxides of nitrogen, 421.
between pure liquid and vapor, 374.
between saturated solution and solid, 393.
between solids and gases, 397.
between water vapor, hydrogen and iron, 401.
calculation of quantities at, 380.
chemical, 71.
complete, 270.
constant, 373.
effect of adding one product on, 381.
effect of change in volume on, 382.
effect of presence of dissociation products, 378.
effect of pressure on, 377 *et seq.*
effect of temperature on, 402.
formulation of, 372.
general law regarding, 285.

Equilibrium, heterogeneous, physical, 374, 376.
van't Hoff's law of mobile, 336.
homogeneous, 376.
homogeneous and heterogeneous, 264.
homogeneous in liquids, 379.
homogeneous in solutions, 382 *et seq.*
in chemical reactions, 371 *et seq.*
in solid phase, 393.
labile, 270.
mobile, 271, 402.
order of, 267, 373.
physical and chemical, 265.
same, approached from either side, 371.
stable and metastable, 268.
Equivalence, 72, 79.
Equivalent conductivities (table), 441.
Equivalent conductivity, calculating, 449.
maximum, 449.
of acetic acid solutions (table), 451.
Equivalent, mechanical, of heat, 36.
Equivalent weight, 44, 60, 78 *et seq.*
Erdmann, 96.
Erg, 31.
Etch figures, 203.
Ether, luminiferous, 110 *et seq.*
Eutectic mixtures, 349.
Evaporation, 278.
Evolution, inorganic, 98 *et seq.*
Exceptions to periodic law, 95.
Exosmosis, 209.
Explanation, 13.
Explosives and dissociation, 174.
Exponents, use of, 524.
External conditions, influence of, 71.
Extinction, photochemical, 507.
Extraction, process of, 351.

FACTORS of energy, 24.
Fahrenheit scale, 33.
Fall in potential, 428.
Faraday, M., 58, 84, 133, 145, 222, 235, 249, 254, 255, 424, 433, 463.
Faraday, the, 433.
Faraday's law, 60, 432 *et seq.*
Faraday's opinion of the atomic theory, 133.
Faraday's tubes of force, 120.
Fehling, 506.
Ferric chloride hydrates, solubilities of, 347 *et seq.*
Feustel, 181.
Figure eight periodic chart, 96.
Findlay, Alexander, 3, 159, 296, 423.
"Firefly," 518.
First law of thermodynamics, 297.
First order reactions, 355.
Fischer, N. W., 209.
Fixation of ions, intensity of, 488.
Fixing negatives, 513.
Fluorescence, 516 *et seq.*
Fluorescent screens, 115.
Flusin, G., 220.
Force, 31.
Formation, heat of, 408.
Formula of hydrogen, 50.
of phosphorus, 50.
Formula volume, 49.
Formula weight, 43, 63.
Formulæ, 41, 43.
empirical, 53.
molecular, 55.
structural, 81 *et seq.*
Formulation, 10.
Formulation of the kinetic theory, 137 *et seq.*
Fraction dissociated, 451.
Fractional distillation, theory of, 308.
Fractions of symbols excluded, 44.
Frauenhofer, J., 103.
Freedom, degrees of, 267.
Free energy, 27.
Free path, mean, of a molecule, 143.
Freezing mixtures, 346.
Freezing point, 23.
determination of, 284, 324.
Freezing-point method, 323 *et seq.*
Freund, Ida, 58, 68.
Freundlich, H., 243, 455.
Friction, internal, *see* Viscosity.
Fundamental definitions, 17.
Fusion, heat of, 408.

GALVANIC cells, 473.
Galvanometer, 425.
Gamma rays, 123, 124.
Gas, 32.
Gas constant, 35.
Gas electrodes, 479.
Gaseous solutions, 206.
Gases, 135 *et seq.*
dissociation of, 170 *et seq.*
liquefaction of, 253 *et seq.*
monatomic, 153.
permanent, 254.
problems, 520.
solution of, 331.
specific heats of, 149.
viscosity of, 189.
Gas laws, 32.
application in problems, 520.
combining to one expression, 34.
exceptions to, 154.
Gas mantle, 100.

Gauss, 181, 509.
Gay-Lussac's gas law, 32.
applied to solutions, 212.
deduction of, 140 *et seq.*
Gay-Lussac's law of combining volumes, 41, 61.
Geissler tubes, *see* Crookes tubes.
Gelatine plates, 510.
"Gels," 246.
Gemberling, 244.
General chemistry, 4.
Generalization, 10.
Genesis of the elements, 97.
Geoffroy, E. F., 69, 71.
Getman, F. H., 159, 423.
Gibbs' phase law, 263 *et seq.*
Glass, colored, 239.
Goldberg, E., 506.
Goldschmidt, 388.
Goniometer, 198.
Graham, T., 243, 244, 249.
Gram, 30.
Gram-centimeter, 31.
Graphic formulæ, 82.
Gravitation analogy, 74.
Gravitation, Newton's law of, 28.
constant, 29.
Gravity battery, 473.
Groth, P., 203.
Grützmacher, 317.
Grunmach, 185.
Guldberg, C. M., 59, 72, 283, 355, 379.
Guthrie, 349.
Guye, P. A., 157, 283.
Gyroscope, 131.

Hale, G. E., 104.
Half period, 126.
Half-shadow polariscope, 227.
Hamburger, H. J., 220.
Hampson, 258.
Hardin, W. L., 254.
Hardness of water, measuring, 462.
Hartley, E. G. J., 212.
Haulefeuille, 376.
Haüy, R. J., 203.
Heat, amount of which can be converted to work, 300.
a mode of molecular motion, 138.
atomic, 65.
capacity, 36, 406.
capacity of one atom, 67.
conduction by dissociated gases, 174.
conduction by gases, 147.
effect, 416.
effect in a wire, 491.
energy, factors of, 404.
evolution of, from radium, 127.
Heat, law of constant, summation, 408.
mechanical equivalent of, 36.
molecular, 66, 150.
motion not electron motion, 140.
nature of, 154.
of combustion of hydrocarbons (table), 416, 417.
of dissociation, 419.
of formation of carbon monoxide, 409.
of formation of dilute solution of ammonium sulphate, 409.
of formation of hydrocarbons (table), 416, 417.
of formation of organic compounds, 414, 415.
of formation of water from its ions, 419.
of liquefaction, 284.
of neutralization, 406, 419.
of organic reactions, 417.
of reaction, 72.
of reaction and formation (table), 412, 413.
of reaction, calculation, from heat of formation, 411.
of solution (table), 413, 414.
of sublimation, 287.
of the earth, 128.
of transformation, 292.
of vaporization, 278, 279.
of vaporization, calculation of, 302.
specific, 35, 36, 65, 66, 67.
specific of gases, 149 *et seq.*
value of change in volume, 415.
value of the gas constant, 415, 416.
wave lengths of, 100.
Heimrod, G. W., 434.
Helium, evolution of, 124.
Helmholtz, 186, 470, 472, 479, 480.
Helmholtz's equation, 492.
Hemihedry, 198.
Henry, 470.
Henry's law, 332.
Dalton's extension of, 333.
exceptions to, 375.
Herz, W., 370.
Hess, G. H., 408, 418.
Hess' law of thermoneutrality, 418.
Heterogeneous chemical equilibrium between solids and gases, 397.
Heterogeneous equilibrium, 264, 374 *et seq.*
Heterogeneous systems, 352.
chemical equilibrium in, 393.
Heydweiller, 460.
Histories of chemistry, 68.
Hittorf, J. W., 113, 442, 449.
Höber, R., 220.
Höpfner's method, 490.

van't Hoff, J. H., 3, 73, 211, 212, 214, 215, 220, 221, 233, 237, 355, 358, 364, 371, 383, 384, 402, 421.
van't-Hoff's law of mobile equilibrium, 336.
Hofmann method, 163.
Hohmann, 382.
Holborn, L., 423.
Homeomorphism, 198.
Homogeneous equilibrium, 264.
in the gaseous phase, 376 *et seq.*
in liquids, 379.
in solid phase, 393.
in solutions, 382.
Homogeneous light, 226.
Homogeneous systems, 352.
Hoppe, E., 494.
Horse power of storage cells, 499.
Horstman, 398.
Hume, D., 13.
Hydrates and thermochemical data, 414.
Hydrogels, 246.
reversible and irreversible, 249.
Hydrogen electrode, 480.
Hydrogen, formula of, 50.
Hydrolysis, 390 *et seq.*
Hydrometer, 175.
Hydrosol, 246.
Hypothesis, 15.

Ice calorimeter, 407.
Identity, 22.
Index of refraction, 190 *et seq.*
Indicators, theory of, 391.
Induced radioactivity, 129.
Induction, 14.
Induction capacity, specific, 463.
Induction, photochemical, 506.
Inertia, 19, 130.
Infinite dilution, 318.
Infracooling, 268.
Inorganic evolution, 98 *et seq.*
"Insoluble," precipitates, 336.
salts, solubility of, 461.
Intensification, 513.
Intensity factor, of chemical energy, 70, 76.
of electrical energy, 466 *et seq.*
of energy, 24.
Intensity of fixation of the ions (table), 488.
Internal friction, *see* Viscosity.
Interstellar space, 140.
Invariant system, 291.
Inversion of sugar, 353.
Inversion point, 292.
Ions, 109, 188.
actual velocity of, 452.
Ions, calculation of velocity of, 453.
color of, 384.
complex, 396, 447.
dissociation into, 222.
independence of, 451.
indicating, 223.
intensity of fixation of, 488.
rate of migration of, 442 *et seq.*
similarity with molecules, 223.
transference numbers of, 447.
velocity of and viscosity of solution, 454.
Isambert, 398.
Isobar, 33.
Isochor, 34.
Isodimorphism, 237.
Isohydric solutions, 458.
Isomers, 84.
Isomorphism, 47, 198, 237.
and analysis, 199.
of elements, 199.
test for, 199.
Isotherm, 32.
Isothermal, compression, 262.
expansion, work done in, 298.
liquefaction, application of phase law to, 267.
Isotherms, Andrews', 154.
Isotonic coefficient, 220.
Isotonic solutions, 211.
Isotropic substances, 200, 202.

Jamin, 150.
Jeans, J. H., 144.
Jevons, 16.
Joly, J., 150.
Joule, J. P., 66, 427.
Joule, the, 405, 427.
Joule-Thomson effect, 259 *et seq.*
Judson, 362.
Jurin's law, 181.

Kauffmann, H., 517.
Kaufmann, W., 131.
Kayser, H., 103.
Kekulé, A., 58, 502.
Kelvin, Lord, see Thomson, Sir William.
Kilowatt, 427.
Kindling temperature, 365.
Kinetic theory, applied to liquids, 175.
applied to osmotic phenomena, 215.
applied to solids, 196.
of gases, 135 *et seq.*
of gases, extension of, 147.
of gases, formulation, 137, 138.
Kinetics, chemical, 352.
Kirchhoff, G. R., 103.
Kirchhoff's law, 104.
Knoblauch, O., 363.

Knowledge, 15.
Kohlrausch, F., 176, 423, 437, 447, 460, 461, 462.
Kohlrausch and Holborn, 441, 457.
Kohlrausch's rule, 449.
Konowalow, 382.
Kopp, F., 282.
Kopp, H., 68, 177, 178, 179, 205.
Kroenig, 136.
Kuenen, J. P., 158.
Kundt's method, 152.

LABILE equilibrium, 270.
Ladenburg, A., 68.
Lævogyratory, 229.
Lambert, 139.
Landolt, H., 30, 236, 241.
Landolt-Börnstein-Meyerhoffer, 162, 423, etc.
Landsberger-Walker-Lumsden method, 318.
Laney, 103.
Langley, S. P., 101.
Laplace, 152, 181.
Lavoisier, A. L., 26, 29, 424.
Law, 10 *et seq.*
Lea, C., 96.
Least stable variety forms first, 295.
Le Bel, 233.
Le Blanc, M., 423, 448, 455, 463, 485, 487.
Le Blanc's method for index of refraction of solids, 192.
Le Chatelier, 73, 399, 402, 421, 503, 504.
Le Chatelier's law, 338, 421, 422.
Le Chatelier-van't Hoff law of mobile equilibrium. 402.
Leclanché cell, 473.
Left rotation, 203.
Lehfeldt, 423.
Lehmann, O., 204.
Lemoine, 376.
Lenard, P., 129.
Length of year proof, 30.
Leucippus, 56.
Lhermite, 219.
Liebig, J., 84, 366.
Light, action of, in photography, 511.
emission of, 515.
emission of, and temperature, 100.
influence of, on reactions, 505.
polarized, 200.
refraction of, 98.
velocity of, 98, 502.
wave lengths of, 99.
Lighting and dissociation, 173.
Linde, 258.
Line spectra, 102.
Lines of force, 86.
Lippmann, 470, 471, 472, 479.
Lippmann's capillary electrometer, 469 *et seq.*
Liquefaction, heat of, 284.
molecular heat of, 285.
of air, 258.
of gases, 253 *et seq.*
Liquid, air, uses for, 261.
crystals, 204.
solutions, 207.
Liquids, 36, 175 *et seq.*
molecular weights of, 64, 185.
the solution of, 334.
Liter, 18.
Lockyer, Sir J. N., 102, 106, 107, 108.
Lodge, Sir Oliver, 129, 452.
Loew, 96.
Logarithms, use of, 521.
Lorentz, H. A., 109, 193.
Lorentz and Lorenz formula, 193.
Lorenz, 65, 193, 465.
Lowering of freezing point, molecular (table), 328 *et seq.*
Lowering of vapor pressure, 310.
and elevation of boiling point, 312.
and osmotic pressure, 327.
Lubrication, 187.
Lüpke, R., 310, 423, 452.
Lüppo-Cramer, 509.
Luminescence, 515 *et seq.*
Luminiferous ether, 110 *et seq.*, 120, 200.
Lumsden, 318.
Lumsden method, *see* Bleier and Kohn.
Luther, R., 423, 506, 509, 511, 513.

Mach, E., 16.
Macnair, 167.
Marckwald, W., 234.
Mariotte, E., 32.
Martin, G., 71.
Mass, 29.
Mass action, law of, 71, 352 *et seq.*
applied to heterogeneous systems, 364.
applied to radioactive change, 125.
formulation, 353.
Mass, apparent, 130 *et seq.*
Mass of a corpuscle, 117, 119.
Masson, O., 453.
Matter, 27, 132.
Maximum osmotic pressure, 210, 212, 213.
Maximum work, 72, 73, 420.
Maxwell, J. Clerk-, 110, 136, 141, 186, 424.
Mayer, Robert, 26.
McGowan, G., 68.
Measurements, electrical, 427 *et seq.*
Mechanical equivalent of heat, 36.

Mechanics, 24.
Mechanics, chemical, 352.
Meldola, R., 509.
Melting may be followed by solidification, 296.
Melting point, 37, 284.
and amorphous solids, 197.
and crystalline solids, 197.
calculation of change in, due to pressure, 304.
effect of pressure on, 288.
Melting points, curve of, 93.
two for one substance, 293.
Membranes, as solvents, 219.
capillary structure of, 219.
copper ferrocyanide, 209.
function of, in osmosis, 218.
giving osmotic effects, 209.
ideal, 209.
semipermeable, 208.
Mendelejeff, D. I., 89, 95.
Menschutkin, N., 367.
Menzies, 170, 322.
Menzies' method, 320.
Mercuric oxalate actinometer, 507.
Mercury, surface tension of, 470.
Mercury unit, 426.
Metamers, 84.
Metaphysics, 9.
Metastable conditions, 286, 345.
cryohydrates, 349.
equilibrium, 268.
forms, formation of, 295.
Meter, 18.
Meth, R., 234.
Metric system and some equivalents, 525.
Metronome, 325.
von Meyer, E., 68.
Meyer, Lothar, 89, 95.
Meyer, O. E., 136, 143, 144, 186.
Meyerhoffer, W., 346.
Michelson, A. A., 19, 98.
Microchemical analysis, 197.
Microns, 252.
Migration of ions, 442 *et seq.*
Mind and instrument, 8.
Miscellaneous data and formulæ, 526.
Mitscherlich, E., 198, 366.
Mixed crystals, classification of, 237.
Mixtures, constant boiling point, 308.
eutectic, 349.
Mobile equilibrium, 271, 402.
van't Hoff's law of, 336.
Molecular conductivity, 439.
formulæ, 55.
heat, 66, 150.
heat of liquefaction, 285.
heat of vaporization, 279.
Molecular lowering of freezing point (table), 328 *et seq.*
motions, possible varieties of, 153.
raising of boiling point, 312.
raising of boiling point, calculation of, 329.
raising of boiling point (table), 330.
refraction, 194.
rotation, 235.
theory, 56 *et seq.*
theory, development of, 61.
volume, 156 *et seq.*
volume of liquids, 177.
volume of solids, 205.
Molecular weight, determination of, 63.
from maximum osmotic pressures, 213.
from surface tension, 184 *et seq.*
of molten metals, 327.
selection of, by covolume, 179.
Molecule, 62, 135.
estimated size of, 144 *et seq.*
Monatomic, gases, 64, 153.
metals, 327.
Monotropy, 296.
Monovariant system, 291.
Morgan, 185.
Morley, 19.
Morse, H. N., 212.
Motion, 19.
Müller-Erzbach, 401.
Muir, M. M. P., 68, 89.
Multiple proportions, *see* Definite and multiple proportions.
Multirotation, 229.
Multivariant system, 292.

Natanson, 378.
Natterer, 255.
"Natural laws," 69.
Negative catalysis, 369.
Nernst, W., 3, 4, 173, 303, 382, 423, 463, 474, 480.
Nernst's theory of production of potential, 474 *et seq.*
Neumann, F. E., 66.
Neumann's extension of Dulong and Petit's law, 66.
Neutrality, thermo, 417.
Neutralization, heat of, 406, 408.
New elements, 125.
Newlands, J. A. R., 89.
Newton, Sir Isaac, 11, 28, 41, 56, 68, 69, 74, 110, 152.
Nickel-iron-alkali cell, 500.
Nicol prism, 201.
Nicol, William, 201.
Niepce, N., 509.
Nollet, Abbé, 209.

Nonreversible cells, 473.
Nonvariant system, 291.
Normal, electrode, 480.
  solution, 207.
Notation, chemical, 39.
Noyes, A. A., 244, 360, 395.
Numerical regularities, *see* Periodic law.

Object, 17.
Objective facts, 8.
  measures, 69.
Octaves, law of, 89, 90.
Odors, transmission of, 136.
Ogdohedry, 198.
Ohm, 426.
Ohm, G. S., 426.
Ohm's law, 426.
Olsen, J. C., 162.
Onnes, K., 261.
Optical, activity, 231.
  axes, 201.
  instruments, 98.
  sensitizing, 513.
  symmetry, 231.
Order of equilibrium, 267, 373.
Order of reactions, determining, 361.
Organic chemistry, classifications of, 85.
Osmosis, qualitative experiment, 208.
Osmotic phenomena and the theory of dissociation, 206 *et seq.*
Osmotic pressure, abnormal, 220.
  abnormality explained, 223.
  and lowering of vapor pressure, 327.
  attempts to explain, 215.
  attraction hypothesis, 216.
  function of the membrane, 218.
  in other solvents than water, 215.
  in solid solutions, 240.
  kinetic hypothesis, 215.
  maximum, 210.
  of colloidal solutions, 252.
  surface tension hypothesis, 217.
  theory of production of potential, 474.
Ostwald-Luther-Drucker, 159, 435, 446.
Ostwald, Wilhelm, 3, 4, 16, 56, 57, 59, 62, 68, 76, 77, 198, 213, 238, 354, 357, 358, 367, 383, 384, 409, 411, 423, 457.
Ostwald, Wolfgang, 243, 246, 455.
Ostwald's dilution law, 383.
  a deduction from, 456.
  and the dissociation constant, 455.
Oxidation and reduction series (table), 484 *et seq.*
Oxides of carbon, 60.
  of copper, 59.
Oxygen the standard for symbol weights, 52.
Ozone, formation of, 422.

Partial pressure, 206.
Partition coefficient, 350.
Paschen, 421.
Pasteur, L., 231, 232, 233.
Pearson, Karl, 12, 13, 16.
Pebal, 171.
Periodic, law, 94.
  system, 87 *et seq.*
  table, 89, 90, 91.
Periods, long, 92.
Perkin, 235.
Permanent gases, 254.
Perpetual motion, 26.
Perpetual motion machines, 403, 503.
Perrin, J., 146, 216, 252.
Petit, A. T., 65.
Pfeffer, W., 210, 211, 212.
Phase, 264.
Phase law, 263 *et seq*, 291, 352.
  applied to solubility of sodium sulphate, 345.
  formulation, 268.
Phenician philosophy, 56.
Philosophy, 5, 8.
Phlogiston, 424.
Phosphorescence, 517.
  physiological, 518.
  without previous illumination, 518.
Phosphorus, formula of, 50.
Photochemical absorption, 504.
  extinction, 507.
  induction, 506.
Photochemistry, 24, 502.
Photography, 24, 248, 508 *et seq.*
Physical chemistry, definition of, 3 *et seq.*
Physical equilibrium, 265, 374, 376.
  processes, 23.
Physicochemical, constants, 23.
  processes, 23.
Physiological phosphorescence, 518.
Pictet, 254, 255.
Pigment process, 514.
Pitchblende, 122.
Planck, M., 306.
Plane polarized light, 200.
Planté, G., 494.
Planté method of forming plates, 494.
Plasmolysis, 211.
Plücker, J., 113.
Plücker tubes, *see* Crookes tubes.
Plus pole, 432.
Poggendorff compensation method, 467.
Poiseuille, 186, 187.
Poiseuille's formula, 186.
Poisson, 181.
Polariscope, 201, 226.
  wedge instrument, 230.
Polarity theory, 74.

Polarization, 485 *et seq.*
at one electrode, 486.
measurement of, 486.
Polarized light, 200.
and solutions, 226.
crystals in, 202.
rotation of plane of, 202.
Polonium, 122, 124.
Polymers, 84.
Polymorphism, 292.
Polymorphous forms, 83, 199.
Pope, W. J., 203.
Positive pole, 432.
Potential, at an electrode, formula, 475.
at contact of solutions, 476.
decomposition (table), 486 *et seq.*
electrode, as a measure of intensity factor of chemical energy, 483.
fall in, 428.
measurement of single, 479.
of calomel electrode, 481.
osmotic theory of, 474.
series (table), 482 *et seq.*
thermodynamic, 296.
Potentiometer, 468.
Poynting, 189.
Precipitation pressure, 331.
Precipitation, the process of, 331 *et seq.*
Predictions from the periodic law, 95.
Prefixes for valence, 80.
Pressure and solubility, 338.
calculation of change in melting point due to, 304.
critical, 256.
dissociation, 398.
effect on equilibrium, 377 *et seq.*
effect on melting point, 288.
effect on viscosity, 188.
of gases, cause, 137.
osmotic, 208.
partial, 206.
vapor, 274 *et seq.*
Preuner, G., 171, 401.
Primary batteries, 472.
Principle, of continuity, 37.
of maximum work, 420.
Printing processes, 514.
Probability, 13, 15.
Problems, applications of the gas laws, 520.
Processes, 22, 253 *et seq.*
chemical, 23.
physical, 23.
physicochemical, 23.
reversible, 27.
temperature coefficient of, 304.
Properties, 17, 135 *et seq.*
number of, 21.
Protecting colloids, 248.
Proto elements, 108.
Protyle, 97.
Proust, J. L., 72.
Prout, W., 87.
Prout's hypothesis, 87, 97, 120, 129.
Pulfrich, 190.
Pulfrich refractometer, 190.
Pure water, 460.
Pycnometer, 175.

QUADRUPLE points, 345.
Quantity factor of energy, 24.

RADIANT energy, 502.
conversion to chemical, 507.
factors of, 504.
pressure exerted by, 503.
Radioactive substances other than radium, etc., 129.
Radioactivity, 121.
induced, 129.
Radium, 122.
heat evolution from, 127.
is it an element, 127.
rays from, 123.
Raising of boiling point, molecular, calculation of, 329.
table of, 330.
Ramsay, Sir William, 3, 103, 124, 125, 142, 185.
Range of alpha rays, 126.
Rankine, W. J. M., 24.
Raoult, 311.
Rate of migration of ions, 442 *et seq.*
Ratio between specific heats of gases, 151.
determination of, 152.
Ratios from analysis, 42, 46.
Rayleigh, Lord, 103, 136.
Reactions, chemical, are all reversible, 372.
equilibria in, 371 *et seq.*
Reactions, determining order of, 361.
endothermic, 422.
heat of, 72, 408.
heat of, calculating, 410.
influenced by light, 505.
in storage cell, 495.
low order of most, 363.
of first order, 355.
of higher orders, 362.
of second order, 356.
of third order, 360.
reversible, 371.
velocity of, 70, 352 *et seq.*
Reaumur scale, 33.
Recurrence of properties, 90.

Reduced equation of conditions, 273.
Reduction and oxidation series (table), 484 *et seq.*
Reduction of acidity by addition of neutral salt, 389.
Refraction, atomic, 194, 195.
  double, 200.
  index of, 190 *et seq.*
  molecular, 194.
Refraction, specific, 193.
Refractometers, 190.
Regularities in boiling points, 282.
Reicher, 383.
Relativity principle, 19.
Remembering, the art of, 8.
Residual current, 488.
Residuum of the unknown, 112.
Resistance, 425.
  in a wire, 491.
  of electrolytes, measuring, 430.
  specific, 438.
Resistivity, 438.
Retarders, in development, 512.
Reversal, of image, 512.
  of spectrum lines, 103.
Reversibility of reactions, 43.
Reversible, cells, 473.
  processes, 27.
  reactions, 371.
Rheostat, 428.
Richard, 150.
Richards, T. W., 167, 180, 407, 434.
Richter, J. B., 72.
Right rotation, 203.
Right thought, 9.
Rigollot, H., 508.
Ripening of emulsions, 510.
Rodger, 188.
Röntgen, W. C., 113.
Röntgen rays, 113, 114, 124.
Roloff, M., 506.
Roozeboom, H. W. B., 296, 347.
Roscoe, 506, 507.
Rosselti, 421.
Rossignol, 362.
Rotary dispersion, 226.
Rotating power, a constitutive property, 228.
  effect of temperature on, 228.
Rotation, electromagnetic, 235.
  molecular, 229, 235.
  of plane of polarized light, 202.
  of pure liquids, 228.
  of solutions, 228.
  right and left, 203.
Rudolphi, M., 384.
Rudolphi-van't Hoff formula, 384, 456.
Rule for formula weight, 49.
Rules, 12.
Rutherford, E., 113, 123, 124, 125, 128, 129.
Rutherford-Soddy hypothesis, 128.
Rutherford's table, 126.

Saccharimeters, 230.
St. Gilles, P. de, 379.
Salcher, 388.
Salts, conductivity of solid and fused, 464.
Saponification of ester, 379.
Saturated compound, 78.
Saunders, A. P., 346.
Scheele, 505.
Schmidt, G. C., 122, 242.
Schmidt, H. W., 127.
Schönfliess, A., 303.
Schreinemakers, F. A. H., 296.
Schupp, W., 171.
Scientific method, 8.
Screens, *see* Fluorescent screens.
Secondary batteries, 472.
Second order reactions, 356.
Seebeck, 509.
Selecting symbol weights, 94.
Selection of symbol weight for oxygen, 44 *et seq.*
Selenium, resistance of, and light, 508.
Semipermeable membranes, 208.
Sending photographs and writing by telegraph, 508.
Sense impression, 8.
Sensitizing, chemical, 514.
  optical, 513.
Separation of optically active varieties, 232 *et seq.*
Series, electrochemical, 73, 482 *et seq.*
Series of spectrum lines, 106.
Shields, 185.
Siedentopf, 145, 251.
Siemens unit, 426.
Silver chloride actinometer, 507.
Single potentials, 479.
Size of a molecule, 144 *et seq.*
Smiles, S., 189.
Smith, Alexander, 12.
Soddy, F., 124, 146.
Sodium sulphate and its hydrates, 340 *et seq*, 345.
Sömmering, 209.
Soluncke, L., 203.
Solar engines, 503.
Solarization, 512.
Solidification may follow melting, 296.
Solids, 36, 196 *et seq.*
  amorphous, 37.
  concentration of, 400.
  crystalline, 37.
  equilibrium in, 393.

Solids, molecular volume of, 205.
molecular weights of, 64.
Solid solutions, 237 *et seq.*
Sols, 249.
Solubilities, mutual, and surface tension, 183.
of ferric chloride hydrates, 347 *et seq.*
Solubility, change of, with pressure, 338.
change of, with temperature, 336.
coefficient of, 332.
critical point of, 334.
curves, 336, 337.
empirical rule regarding, 335.
increasing the, 396.
nothing insoluble, 479.
of "insoluble" precipitates, 461.
of sodium sulphate, 340.
Solubility product, 394 *et seq.*
exceptions to, 395.
formulation of, 395.
Solute, 36.
Solution, heat of, 339, 408, 413 (table), 414.
in part a chemical reaction, 339.
of gases, 331.
of liquids, 334.
pressure, 331.
the process of, 331 *et seq.*
Solutions, 36.
classification of, 206 *et seq.*
colloidal, 37.
conductivity of nonaqueous, 462.
continuity in, 37.
homogeneous equilibrium in, 382.
isohydric, 458.
isotonic, 211.
normal, 207.
of gases in solids, 238.
of liquids in solids, 238.
of solids in solids, 237.
potential at contact of, 476 *et seq.*
salt, viscosity of, 188.
solid, 237.
surface tension of, 184.
which rotate the plane of polarized light, 228.
Solvent, 36.
influence of, on the velocity of reaction, 366.
Space, 17.
between molecules, 64.
Specific, cohesion, 182.
conductance, 438.
density, 31.
gravity, 23, 31.
heat, 35, 36, 65, 66, 67.
heats of gases, 149 *et seq.*
induction capacity, 463.
refraction, 193.
Specific, resistance, 438.
rotation, *see* Rotation, specific.
viscosity, 187.
volume, 31.
volume of liquids, 176.
Spectra, absorption, 103.
and the periodic law, 107.
band, 105.
line, 102.
of argon, hydrogen, iron, 106.
of compounds, 105.
Spectrometer, 190.
Spectroscopic analysis, 102.
delicacy of, 105.
Spectroscopic evidences, 98 *et seq.*
Spectrum, 99, 136.
Spectrum lines, formulation of series, 106.
Spencer, Herbert, 18.
Spinthariscope, 123.
Spontaneous combustion, 365.
Stability of elements, 129.
Stable equilibrium, 268.
Stahl, G. E., 70.
Standard cells, 468 *et seq.*
Standard conditions, 34.
Star temperatures, 102.
Stas, J. S., 87.
Static method for measuring vapor pressures, 274 *et seq.*
Statics, chemical, 352.
Steam calorimeter, 407.
Steele, B. D., 453.
Stefan, J., 101.
Stefan's law, 101.
Stellar chemistry, 104.
Steno, N., 198.
Stereochemistry, 233.
Stevenson, 185.
Stieglitz, J., 392.
Stoicheiometrical constants, 40.
Stoicheiometry, 39.
Stokes, 186.
Stokes' laws, 118, 517.
Stoney, G. J., 132, 147.
Storage cells, 473, 494 *et seq.*
efficiency of, 497.
horse power of, 499.
rules for charging and discharging, 497.
"sulphated," 498.
temperature coefficient of, 499.
ways to damage, 498.
Strength, of acids, 72, 385.
of oxidizing and reducing agents, 484
Stretched seconds, 20.
Structural formulæ, 81 *et seq.*
Structure of atom, 109.
Strutt, R. J., 87.

Subjective facts, 8, 9.
measures, 69.
Sublimation, 287.
Submicrons, 252.
Substance, 22.
Substitution rule, 60.
Sugar analysis, 230.
"Sulphated" storage cells, 498.
Sun's energy, 503.
spectrum, 100.
Supercooling, 268.
experimental demonstration of, 286.
Superheating, 269.
Supersaturation, 269.
Surface tension, 180 *et seq.*
and molecular weights, 184 *et seq.*
hypothesis regarding osmotic pressures, 217.
of mercury, 470.
Symbols, 43.
Symbol weights, 43, 57, 63.
application of Dulong and Petit's law to selecting, 65.
correcting, 94.
selection of, 42 *et seq*, 94.
table of, 54.
System, 26, 263.
Systems of crystals, Weiss', 197.

TABLE of symbol weights, 54.
Temperature, and density of liquids, 176.
and solubility, 336.
and velocity of reaction, 364.
Temperature coefficient, of calomel electrode, 482.
of cells, 491.
of processes, 304.
of standard cells, 469.
of storage cells, 499.
of transference numbers (table), 450.
Temperature, critical, 255.
effect of, on equilibrium, 402.
estimation of, by light emitted, 100.
kindling, 365.
of electric arc, 421.
of sun, 421.
of stars, 102.
Tension, surface, *see* Surface tension.
Tetartohedry, 198, 232.
Theoretical chemistry, 4.
value of, 5 *et seq.*
Theory, 6 *et seq*, 10, 14.
comparison of law and, 16.
nature of, 14.
of fractional distillation, 308.
of indicators, 391 *et seq.*
use of, 15.
Thermal unit, British, 405.
Thermochemical data, 404 *et seq.*
Thermochemistry, 24, 253, 404 *et seq.*
first law of, 408.
Thermodynamic potential, 296.
Thermodynamics, 24, 297 *et seq.*
first law of, 26, 297.
second law of, 27.
Thermoelements, 493.
Thermoluminescence, 516.
Thermometers, 35.
Beckmann, 408.
Thermoneutrality, 417.
Thiel, A., 393.
Thilorier, 254.
Third gas law, 34.
Third order reactions, 360.
Thompson, S. P., 424.
Thomsen, Julius, 72, 73, 404, 420.
Thomson, J. J., 109, 112, 113, 116, 117, 119, 120, 131.
Thomson-Joule effect, 259.
Thomson, Thomas, 59.
Thomson, William (*Lord Kelvin*), 7, 75, 111, 139, 144, 145.
Thorpe, T. E., 68, 188.
"Ties," 85.
Time, 18.
Tin pest, 295.
Tin, transformation of, 294.
Titoff, A., 367.
Tolman, R. C., 20.
Total energy, 26.
Tourmaline polariscope, 202.
Transference numbers (tables), 447, 450.
Transformation point, 292.
Transformations, heat of, 292.
of sulphur, 293.
of tin, 294.
velocity of, 295.
Transition points, 292 *et seq*, 341 *et seq.*
determination of, 292.
unknown, 295.
Transport numbers of ions (tables), 447 450.
Traube, J., 179, 180, 184.
Traube, M., 209.
Trautz, M., 505, 518.
Triads, Doebereiner's, 88, 92.
Triboluminescence, 516.
Triple point, 289 *et seq.*
Trouton's law, 283.
"True" solutions, 245.
Two melting points, 293.
Tyndall effect, 250 *et seq.*

ULTIMATE constituents, 39, 57, 134.
Ultramicroscopic method, 146, 250.
Unimolecular reactions, 355.

Unit for symbol weights, 44.
Unit quantities of chemistry, 39.
  selection of, 42 *et seq.*
Unit quantity of electricity, 222, 433.
Univariant system, 291.
Uranium and radium, proportions of, 126.
Use of arrows, 43.

VACANT spaces in periodic table, 95, 129.
Vacuum jacketed vessels, 259.
Valence, 58, 68, 77 *et seq.*
  and charge on an ion, 222.
  and electron theory, 425.
  and electrons, 132.
Value of physical chemistry, 5.
Vapor densities, 159 *et seq.*
  abnormal, 170.
Vapor density methods, 63, 159 *et seq.*
Vaporization, calculation of heat of, 302.
  heat of, 278, 408.
  molecular heat of, 279.
Vapor or gas, 256.
Vapor pressure, 274 *et seq.*
  and surface tension, 184.
  and temperature, 275.
  at the melting point, 285.
  curves, 276.
  dynamic method of measuring, 281.
  kinetic theory and, 277.
  lowering and boiling point, 312.
  lowering and freezing point, 323.
  lowering and temperature, formulation, 310.
  of solutions, 307 *et seq.*
  of water, ice, alcohol, ether, 275.
  phase law and, 276.
  static method of measuring, 274.
Vapor tension, 274.
Varying valence, 80.
Velocity, 19.
  constant, 353.
  of chemical reactions, 352 *et seq.*
  of corpuscles, 117.
  of ions, 442 *et seq.*
  of ions, actual, 452.
  of ions and viscosity, 454.
  of ions, calculation of, 453.
  of light, 19, 502.
  of molecules, 143.
  of reaction, 70.
  of reaction and temperature, 364.
Velocity of reaction, catalytic effects on, 366.
  of reaction, influence of solvent, 366.
  of transformation, 295.
Victor Meyer method, 165 *et seq.*
da Vinci, Leonardo, 181, 509.
Viscosimeters, 186 *et seq.*
Viscosities (table), 187.
Viscosity and velocity of ions, 454.
Viscosity or internal friction, 186 *et seq.*
Viscosity of solids, 196.
Vogel, H. W., 509, 513.
Volt, 427.
Volta, 427.
Voltaic cells, 473.
Voltaire, 22.
Voltameter, 433.
Volume, atomic, curve of, 92, 93, 177.
  effect of change in, on equilibrium, 382.
  formula, 49.
  heat value of change in, 415.
  molecular of liquids, 177.
  molecular of solids, 205.
  specific, of liquids, 176.
Volumes, law of combining, 41.
Vortex rings, 110 *et seq.*

Waage, P., 59, 72, 355, 379.
van der Waals, 11, 136, 154, 157, 272.
van der Waals' equation, 155, 175, 177.
  application of, 270.
Walden, P., 462, 464.
Walker, J., 318, 362.
Warder, R. B., 357.
Water, as a catalytic agent, 368.
  calorimeter, 406.
  degree of dissociation of, 461.
  measuring hardness of, 462.
  of crystallization, 400 *et seq.*.
  pure, 460.
Waterston, J. J., 136.
Watt, James, 427.
Watt, the, 427.
Wave lengths, of light, 99.
  table of, 100.
Weber, 509.
Webster, 7.
Weight, 28, 29.
  equivalent, 44, 60, 78 *et seq.*
  law of definite and multiple proportions by, 40.
  molecular, 63.
  symbol (table), 54.
Weiss, 197.
Weiss' crystal systems, 197.
Welsbach mantle, 241.
Wenzel, K. F., 70, 71, 352, 355.
Weston standard cell, 468.
Wet plate process, 509.
Wheatstone, C., 429.
Wheatstone bridge, 429.
Whetham, W. C. D., 127, 453.
Whewell, W., 9.
Widal test, 248.

Wien, W. C. W., 101, 120.
Wien's law, 101.
Wilhelmy, L., 353, 354, 355.
Wilsmore, N. T. M., 482, 488.
Wilson, C. T. R., 118.
Wilson, H. A., 119.
Wöhler, F., 84.
Woker, G., 370.
Wollaston, W. H., 59.
Words and ideas, 9.
Work, 30.
  and heat, 300.
  done by gas expanding isothermally, 298.
  maximum, 72, 73, 420.
X-RAYS, 113, 114, 115, 124.
  nature of, 120.

Young, Sidney, 3, 283.

Zeeman, P., 109.
Zeeman effect, 108, 109.
Zeolites, 238.
Zero, absolute, 138.
  electrode, 480.
Zinc standard cell, 469.
Zirkel, F., 238.
Zsigmondy, 145, 243, 251.

JAN 19 1916